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Organic Chemistry.

The Lubricant and Asphaltic Hydrocarbons in Petroleum. C. F. Mabery (*Ind. Eng. Chem.*, 1923, **15**, 1233—1238).—Most crude petroleums begin to show evidence of decomposition at a temperature of 300° even at 20 mm. pressure. In an investigation of the hydrocarbons boiling above this point, applied to samples of crude petroleum of varying origin, separation was therefore effected by means of fractional solution in a mixture of ether and ethyl alcohol. The fractions so obtained were examined as to density, mol. weight (as determined by solution in stearic acid at 50°), and composition by analysis. In all cases, these heavy hydrocarbons fall into one of two classes (*D*) hydrocarbons, lubricants throughout, and (*H*) hydrocarbons of which the heavier are asphaltic. The latter are usually poorer in hydrogen, the series identified through the whole range of samples varying from C_nH_{2n-4} to C_nH_{2n-20}. The halogens react normally with these hydrocarbons. The nitro-derivatives of the (*D*) hydrocarbons separate as finely divided crystals, those of (*H*) hydrocarbons as oils when poured into water. These derivatives have much lower mol. weights than the original oils and are nitro-carboxylic acids. All samples of fractions from American petroleum were found to contain carboxylic acids or esters in proportions ranging from traces up to 2%. This probably accounts for irregular variations in the density of succeeding fractions. Iodine number determinations show that only the ring type of unsaturation exists in lubricant hydrocarbons. [Cf. *B.*, Feb.] C. I.

The Processes of Dehydrogenation in the Presence of Catalysts. J. K. Pfaff and R. Brunck (*Ber.*, 1923, **56**, [*B*], 2463—2464).—The catalyst is prepared by mixing solutions of sodium aluminate and nickel nitrate and rendering the precipitation complete by passing carbon dioxide to saturation. The paste is mixed with pure, ignited aluminium oxide, filtered, and washed as free as possible from alkali. It is subsequently dried and reduced by hydrogen at 320°. In the presence of this material, benzene is smoothly hydrogenated at 180—200° to hexahydrobenzene, but, unexpectedly, the latter substance is not reconverted into benzene to more than a minimal extent at any temperature below about 500°. Purified lignite tar oil, b. p. 80—150°, is similarly readily saturated with hydrogen at 180—200°, but, under the conditions used in the attempted dehydrogenation of hexahydrobenzene, the product is converted quantitatively into methane. Under similar conditions, a purely aliphatic fraction of American petroleum yields almost entirely methane and leaves a small carbonised deposit on the catalyst; the reaction commences at about 240° and is almost quantitative at 260°.

By means of the nickel catalyst, the aliphatic components can readily be removed as methane from a mixture of aliphatic hydrocarbons and naphthenes. H. W.

Addition of Nitrogen Trichloride to Unsaturated Hydrocarbons. I. G. H. COLEMAN and H. P. HOWELLS (*J. Amer. Chem. Soc.*, 1923, **45**, 3084—3089; cf. A., 1922, i, 133).—Nitrogen trichloride was added slowly to a solution of Δ^{β}-butene in carbon tetrachloride at −10°, and after washing and removal of water the β-chloro-γ-dichloroaminobutane formed, NCl_2·CHMe·CHMeCl, was reduced by concentrated hydrochloric acid to β-chloro-γ-aminobutane, NH_2·CHMe·CHMeCl; the *benzoyl* derivative, colourless needles, m. p. 105—106°, was isolated. Similar reactions with Δ^{α}-butene resulted in the isolation of *r*-α-chloro-β-benzamidobutane, slender, silky needles, m. p. 91—92°, which was reduced to *r*-β-benzamidobutane, m. p. 84—85°. The latter substance was also prepared from methyl ethyl ketoxime, and it had the same melting point (Pope and Gibson, T., 1912, **101**, 1702). β-*p*-Nitrobenzamidobutane obtained from Δ^{α}-butene and from methylethylketoxime melted at 114·5—115·5°. Nitrogen trichloride reacted rapidly with β-methyl-Δ^{β}-butene; no amine was produced but amylene dichloride and chloroamylene chloride were formed. F. B.

Acetylene Condensations. II. The Theory of the Formation of Cuprene. H. P. KAUFMANN and W. MOHNHAUPT (*Ber.*, 1923, **56**, [*B*], 2533—2536).—The conversion of acetylene into cuprene in the presence of copper or copper compounds at 230—300° does not take place in the complete absence of oxygen. The product is not homogeneous, the composition varying between $(C_{11}H_{10})_x$ and $(C_{15}H_{10})_x$. In addition, small amounts of oily compounds are produced. The colour of the product ranges from pale yellow to dark brown. The authors consider that its formation is due to the production of an intermediate additive compound of acetylene with cuprous or cupric oxide which immediately undergoes pyrogenic decomposition. Possibly the variation in temperature due to the rapid stream of gas plays a distinct part. Since the oxide which is regenerated by decomposition of the acetylide again takes part in the reaction, the proportion of oxygen present (in the case of copper) need not be great. The formation and decomposition of the acetylide explains the peculiar observation that the copper catalyst which originally lies at the bottom of the vessel ultimately becomes distributed throughout the whole reaction chamber. The superiority of copper over other metals as a catalyst is ascribed to the possibility of the simultaneous production of oxide and acetylide. The liberated acetylene must be endowed with particular reactivity, as a consequence of which the reactions which occur are much more profound than those involved in the pyrogenic decomposition of acetylene alone and lead through the most stable forms of combination to the inactive cuprene, the purely aromatic nature of which is thus readily explained (cf. Kaufmann and Schneider, A., 1922, i, 245). H. W.

Process for Converting Halogen Substitution Products of Hydrocarbons into Hydrocarbons, or other Halogen Substitution Products of Hydrocarbons, containing a Higher Number of Carbon Atoms. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (Brit. Pat. 196272).—The process consists in passing halogen substitution products of hydrocarbons, or mixtures of them, in the presence of water, over a catalyst comprising metals (*e.g.*, platinum) or their compounds (*e.g.*, thorium oxide, zirconium chloride, bismuth oxide, stannic chloride, zinc chloride), or non-metals (*e.g.*, charcoal), carried on porous materials (particularly active charcoal), at an elevated temperature not exceeding 400°. Details are given for the production of ethyl chloride and ethylene from methyl chloride and of ethylidene chloride from a mixture of methyl chloride and methylene chloride. [Cf. *B.*, Feb.] W. T. K. B.

Some Constants of Ethyl Chloride. E. DEISS (*Z. Elektrochem.*, 1923, **29**, 586—587).—The ignition temperature of ethyl chloride lies below −18·5°, the lower limit of explosion for mixtures of air and ethyl chloride is found with the mixtures containing 3·6% of ethyl chloride, the upper limit being the mixture containing 11·2%, and the maximum explosion occurs with 6·5% of ethyl chloride. J. F. S.

Auto-oxidation of Chloroform. A. M. CLOVER (*J. Amer. Chem. Soc.*, 1923, **45**, 3133—3138).—When chloroform was exposed to diffused light it developed acidity and oxidising power. The latter reached a maximum and then decreased, whilst the acidity continued to increase. On dilution with water, the oxidising substance reacted to form hydrogen peroxide. The oxidising substance is probably dichlorocarbon peroxide, CO_2Cl_2. The addition of petroleum, alcohol, phenol, and many other substances inhibits the decomposition of chloroform, but the mechanism of their action remains obscure. Bromoform and methylene chloride also develop oxidising substances on standing. F. B.

The Synthesis of Higher Members of the Aliphatic Series from Carbon Monoxide. F. FISCHER and H. TROPSCH (*Ber.*, 1923, **56**, [*B*], 2428—2443).—An examination of the possibility of the conversion of water gas into motor spirit. In the presence of a suitable catalyst, carbon monoxide is reduced by hydrogen to a mixture of alcohols, ketones, aldehydes, etc., which is designated "synthol." It is converted when heated under pressure into a mixture of hydrocarbons, to which the name "synthin" is assigned. In a somewhat similar manner, the direct production of hydrocarbons from mixtures of carbon monoxide and hydrogen has been patented by the Badische Anilin- & Soda-Fabrik (D.R.-P. 293787, 295203, and 295202); the different course of the reaction is possibly due to the fact that technical water gas containing carbon dioxide and an excess of hydrogen over carbon monoxide is used in the experiments now described, whereas in the work of the Badische Anilin- & Soda-Fabrik the carbon monoxide was invariably in excess.

[With W. KRÖNIG.]—Technical water gas is freed as far as possible from compounds of sulphur, compressed at 150 atmospheres and heated at 400—450° in the presence of iron covered with potassium carbonate; the product of the reaction separates into an aqueous and an oily layer in the volume proportion 2 : 1. A marked difference in the components of the two phases is not observed. Each consists of fatty acids, aliphatic aldehydes, ketones, and alcohols; in addition, the oily layer contains esters and hydrocarbons in small amounts. The presence of formic, acetic, propionic, and *iso*butyric acids is established. Higher fatty acids are also present which have not been identified individually; as judged by equivalent and boiling point, acids of the formula $C_8H_{16}O_2$ are produced. The presence of propaldehyde, probably *n*-butaldehyde and *iso*butaldehyde, is established, whereas formaldehyde could not be detected. The ketones comprise acetone, methyl ethyl ketone, diethyl ketone, and methyl *n*-propyl ketone. Methyl, ethyl, and *n*-propyl alcohols are identified in addition to higher homologues. The esters have not been identified. Hydrocarbons are present only in minor amount (about 2%).

The conversion of synthol, b. p. 99—225°, into synthin is effected under pressure at 400—450° in an autoclave in an atmosphere of nitrogen. The liberated gas consists of carbon dioxide (14·5%), hydrocarbons soluble in fuming sulphuric acid (22·7%), oxygen (0·7%), carbon monoxide (14·6%), hydrogen (9·6%), paraffin hydrocarbons (21·8%), and nitrogen (16·1%). The liquid product consists mainly of hydrocarbons which boil over a wider range than the initial material. They are stable towards concentrated sulphuric acid, and therefore saturated. The atomic ratio, C : H, increases from the fractions of lowest to those of highest boiling point. Whereas in the former this ratio is nearly 1 : 2, as is required for the simpler naphthenes, in the latter its value indicates that only saturated hydrocarbons with several condensed ring systems can be present. Possibly, the process consists in the initial conversion of the alcohols by loss of water into olefines which become further subdivided into small portions which unite to form naphthenes.

The theory of the experiments is discussed in detail. It is pointed out that the presence of a hydrogen carrier such as iron, nickel, cobalt, or, possibly, manganese, is essential, in addition to a base or the salt of a base with a weak acid. Apparently the production of oil is favoured by the strength of the base, which, however, by itself (*e.g.*, potassium hydroxide in the presence of pumice) is not sufficient. It appears most probable that the initial product is formaldehyde, which in the absence of bases passes into methane; in the presence of the latter, however, it becomes converted into methyl alcohol, as is established by the production of large amounts of the latter from paraformaldehyde and hydrogen at 400° under 100 atmospheres in the presence of pumice loaded with potassium carbonate. Methyl alcohol is converted by carbon monoxide, either directly or through methyl formate, into acetic acid, the stepwise reduction of which gives

acetaldehyde and ethyl alcohol, whilst its catalytic decomposition gives acetone. An extension of this operation yields propionic acid, propaldehyde, *n*-propyl alcohol, and diethyl ketone. The non-production of members containing more than seven or eight carbon atoms is due to their instability under the experimental conditions. The production of higher alcohols is probably due to loss of water from the simpler members of the series. H. W.

Alcohols and Hydrocarbons from Beeswax. GASCARD and G. DAMOY (*Compt. rend.*, 1923, **177**, 1442—1443; cf. this vol., i, 8).—The following alcohols (2 and 4 in largest quantity) have been obtained from beeswax, after alkaline hydrolysis: (1) *Neoceryl*, $C_{25}H_{52}O$, m. p. 75·5°; (2) ceryl, $C_{27}H_{56}O$, m. p. 80°; (3) *montanyl*, $C_{29}H_{60}O$, m. p. 84°; and (4) myricyl alcohols, $C_{31}H_{64}O$, m. p. 87°. After crystallising the alcohols, the following hydrocarbons were obtained from the mother-liquors: Pentacosane, $C_{25}H_{52}$, m. p. 54—54·5°; heptacosane, $C_{27}H_{56}$, m. p. 59·2—59·5°; nonacosane, $C_{29}H_{60}$, m. p. 63·5°, and hentriacontane, $C_{31}H_{64}$, m. p. 68·4—69°. All the acids, alcohols, and hydrocarbons obtained from beeswax crystallise in hexagonal plates. E. E. T.

Δ^{α}-Pentene-γ-ol [Ethyl Allyl Alcohol]. J. BAUDRENGHIEN (*Bull. Soc. chim. Belg.*, 1923, **32**, 337—339; cf. A., 1922, i, 710; also Delaby, A., 1923, i, 741).—The following physical constants are given: b. p. 114·2—114·4°/753 mm., d_4^{20} 0·8373, n_D^{20} 1·4254. Dry hydrogen chloride is absorbed by the alcohol, yielding a mixture of products one of which, believed to be CH_2:CH·CHEtCl, has b. p. 93—94°/759·8 mm., d_4^{20} 0·8978, n_D^{20} 1·4254. This substance reacts with potassium acetate with formation of a mixture of isomerides. Hydrogen bromide gives with the alcohol a product, b. p. 124—131°, which is very unstable. H. J. E.

Molecular Conductivity of Potassium Iodide in Epichlorohydrin. N. A. YAJNIK and B. R. SOBTI (*J. Amer. Chem. Soc.*, 1923, **45**, 3138—3139).—The molecular conductivity of potassium iodide in epichlorohydrin was determined by the Kohlrausch method. The results are: mol. volume (litres), 60, 120, 240, 480; specific conductivity 10 mhos, 2·3, 1·3, 0·8, 0·53; mol. conductivity (mhos), 13·8, 15·6, 19·2, 25·4, respectively. F. B.

Carbohydrates and Polysaccharides. V. Use of Acetylene for the Synthesis of Cyclic Acetals. H. S. HILL and H. HIBBERT (*J. Amer. Chem. Soc.*, 1923, **45**, 3108—3116; cf. A., 1923, i, 439, 753).—The following cyclic acetals were prepared by passing acetylene into a mixture of a polyhydroxy-compound and a small amount of mercuric sulphate with 93% sulphuric acid. Ethylidene trimethylene ether, b. p. 108—111°, ethylidene αβ-propylene ether, b. p. 92°; *ethylidene glycerol bromohydrin*, b. p. 170—182°; ethylidene glycerol, b. p. 189—196°; *ethylidene αδ-tetramethylene ether*, a colourless liquid, b. p. 124—127°; *ethylidene pinacol*, b. p. 133—134°; *β-methylpentane-βδ-diol ethylidene ether*, b. p. 139—140°; *monoethylidene α-methyl glucoside*, silky,

colourless crystals, m. p. 77°, and ethylidene glucose. The mechanism of the reaction is discussed. F. B.

Carbohydrates and Polysaccharides. VI. Relative Ease of Formation of Five- and Six-membered Heterocyclic Carbon–Oxygen Configurations. H. S. HILL and H. HIBBERT (*J. Amer. Chem. Soc.*, 1923, **45**, 3117—3124; cf. preceding abstract).—When one equivalent of acetylene was passed into a mixture of one equivalent of ethylene glycol and one equivalent of trimethylene glycol, the proportion of ethylidene ethylene ether (five-membered ring) to ethylidene trimethylene ether (six-membered ring) was 1 : 2. A similar result was obtained in the case of a mixture of propylene αβ-glycol and trimethylene glycol, whilst with a mixture of ethylene glycol and β-methylpentane-βδ-diol the ratio was 1 : 5. Using a mixture of trimethylene glycol and β-methylpentane-βδ-diol, the ratio of the two six-membered ring derivatives was 1 : 2. Thus the six-membered ring compound was formed in preference to the five-membered ring compound, and the presence of methyl groups attached to the glycol carbon atoms favours ring formation. Similar partition experiments with mixtures of glycerol and ethylene glycol led to the conclusion that ethylidene glycerol consists of a mixture of $CHMe<^{O\cdot CH\cdot CH_2\cdot OH}_{O\cdot CH_2}$ and $CHMe<^{O\cdot CH_2}_{O\cdot CH_2}>CH\cdot OH$, the latter predominating. F. B.

Carbohydrates and Polysaccharides. VII. The Ease of Formation and Nature of certain Six-, Seven-, and Larger Carbon–Oxygen Cyclic Structures. H. S. HILL and H. HIBBERT (*J. Amer. Chem. Soc.*, 1923, **45**, 3124—3132; cf. preceding abstract).—The partition of one equivalent of acetylene between one equivalent each of ethylene glycol and tetramethylene glycol shows that the five-membered cyclic acetal is formed three times as readily as the seven-membered compound. Attempts to prepare the cyclic ethylidene derivatives of octa- and deca-methylene glycols resulted in syrupy, odourless acetals with very high and indefinite boiling points. The tendency of atomic chains to assume spiral ring formation is discussed. F. B.

Preparation of Chloroethylsulphuryl Chloride. CHEMISCHE FABRIK VORM. WEILER-TER MEER (D.R.-P. 374141; from *Chem. Zentr.*, 1923, iv, 720).—Ethylene chloride is treated with fuming sulphuric acid with or without a catalyst and the resulting *chloroethylsulphuryl chloride*, a colourless, heavy oil with an odour like that of formaldehyde, b. p. 120—122°/80 mm., is obtained by first separating through addition of ice-water and then distilling in a vacuum. *Dichlorodiethyl sulphate*, b. p. 180—182°/60 mm., is also obtained. G. W. R.

Noteworthy Behaviour of Organic Sulphur Compounds towards Sodium Arsenite. A. GUTMANN (*Ber.*, 1923, **56**, [*B*], 2365—2367).—The mode of combination of sulphur in certain organic (and inorganic) compounds can be distinguished by their

behaviour towards sodium arsenite. Those which convert the arsenite into sodium thioarsenate, Na_3AsSO_3, contain sulphur in the polysulphide form; these also convert cyanide into thiocyanate; those compounds which, through the intermediary action of water, oxidise the arsenite to arsenate, contain sulphur in the persulphide form, corresponding with the peroxide form of oxygen. Dixanthogen disulphide, diacetyl disulphide, and cupric sulphide all belong to the first class; tin disulphide and ultramarine, however, contain sulphur only in the bivalent form and are not reactive. Diamyl disulphide, diphenyl disulphide, dithio-*N*-dimethylaniline and phenyl ethyl disulphide all oxidise arsenite to arsenate and are reduced to mercaptans; they contain one atom of persulphide sulphur. Methyl trisulphide with sodium arsenite gives both arsenate and thioarsenate, and is reduced to methyl mercaptan; it therefore contains one atom each of polysulphide- and persulphide-sulphur. The free thiocyanogen of Söderbäcks (A., 1920, i, 219) and the phenylthiolthiocyanate of Lecher and Wittwer (A., 1922, i, 641) both contain 1 atom of persulphide sulphur, whilst the disulphur dithiocyanate of the same authors contains 2 atoms of polysulphide and 1 atom of persulphide sulphur. When cupric thiocyanate is heated with sodium arsenite, a green precipitate is first formed which, on boiling, changes into red cuprous oxide, arsenate being formed. In acid solution, white cuprous thiocyanate and arsenate are formed. In this reaction, the formation of cuprous salt is not due to the reducing action of the arsenite; this is oxidised to arsenate by the thiocyanic acid formed when the cupric salt is heated. E. H. R.

The Stereoisomerism of Brassidic and Erucic Acids. D. Holde (*Ber.*, 1923, **56**, [*B*], 2405).—A claim of priority in this field against von Auwers (cf. A., 1923, i, 294). E. H. R.

A New Unsaturated Fatty Acid in Sperm and Dolphin Oils. M. Tsujimoto (*J. Chem. Ind. Japan*, 1923, **26**, 608—620).—By the bromo-ester method of Grün and Janko (*Z. deut. Oel-Fett Ind.*, 1921, 553, 572) and the lead salt–light petroleum method, a new *tetradecenoic acid*, $C_{14}H_{26}O_2$, has been isolated from sperm and dolphin oils, the amount being about 3% of the material. The acid was found to be chiefly responsible for the iodine absorption of the lower fractions of the methyl esters. It is a colourless liquid, b. p. 172°/5 mm., d_4^{15} 0·9079, n^{15} 1·4566, iodine value 106·8 (*methyl* ester, b. p. 140°/5 mm., *barium* salt, a white powder), and gives myristic acid, $C_{14}H_{28}O_2$, by reduction with hydrogen in the presence of platinum black, and dihydroxymyristic acid, $C_{14}H_{26}(OH)_2O_2$, m. p. 118—119°, by oxidation by Hazura's method. By oxidising with potassium dichromate and sulphuric acid, the acid gave nonoic acid. On treating the acid with ozone in a chloroform solution, an ozonide peroxide, $C_{14}H_{26}O_2$, was obtained as a viscid, colourless liquid, the decomposition of which with water gave nonaldehyde, nonoic acid, glutaric acid semialdehyde (?), and glutaric acid. From these facts, it is concluded that the formula is $CH_3{\cdot}[CH_2]_7{\cdot}CH{:}CH{\cdot}[CH_2]_3{\cdot}CO_2H$. K. K.

Preparation of the Highly Unsaturated Acids of Fish Oils. M. Tsujimoto and Kanesuke Kimura (*J. Chem. Ind. Japan*, 1923, **26**, 891—893).—The lithium salt–acetone method of Tsujimoto (A., 1921, i, 78) for the separation of highly unsaturated acids is applicable to the quantitative analysis of the acids, but unsuitable for the preparation of the acids, owing to the need of large amounts of acetone and lithium hydroxide; a modification of the method is therefore proposed for the latter purpose. The fatty acids from fish oil (10 g). are dissolved in acetone (95 c.c.), neutralised with ammonia and mixed with an aqueous solution of the equivalent amount of lithium acetate or chloride, the sulphate not being suitable for the purpose owing to its smaller solubility in water. The amount of water is kept such that the resulting acetone solution is of 95% strength. It is well shaken for thirty minutes and then cooled in ice-water for one hour. Highly unsaturated acids are dissolved, chiefly as ammonium soaps, and the lithium salt acts as the precipitant for less unsaturated acids. The solution is filtered through a dry filter-paper in a cold funnel. After evaporation of the solvent, the residue is treated with a dilute mineral acid and thus highly unsaturated acids are isolated. The yield of the acids by this method is less than that by the peroxide method, but the properties of the products are almost the same. K. K.

The Decarboxylation of Dimethylpyruvic Acid and its Preparation. H. K. Sen (*Biochem. Z.*, 1923, **143**, 195—200).—Dimethylpyruvic acid (α-keto*iso*valeric acid) was obtained by the following process, used in preference to the method described by Rassow and Bauer (A., 1909, i, 632). Ethyl *iso*propylacetoacetate was treated with dry ethyl nitrite gas in the presence of sodium ethoxide, and, from the resulting sodium derivative, the oxime of ethyl dimethylpyruvate was obtained and purified by distillation in a vacuum. From the oxime, dissolved in 85% formic acid and treated with nitrosyl sulphuric acid, ethyl dimethylpyruvate together with the free acid was obtained. Hydrolysis of the ester with 5% aqueous potassium hydroxide yielded dimethylpyruvic acid boiling at 76—78°/11 mm. The semicarbazone (prismatic needles) had m. p. 102—103°. Dimethylpyruvic acid in the presence of phosphate buffer mixtures is fermented by preparations of dried yeast to give *iso*butaldehyde in 50% yield. A 75% yield of the aldehyde is obtained when the fermentation is carried out in the presence of acetate and sodium sulphite. *iso*Butyl alcohol is not formed in detectable amount. J. P.

Keto-enolic Tautomerism. II. The Combined Application of Chemical Methods to the Estimation of Enols. H. P. Kaufmann and G. Wolff (*Ber.*, 1923, **56**, [*B*], 2521—2526; cf. A., 1922, i, 985; 1923, i, 90).—Fission of the dienolic form of ethyl diacetylsuccinate by ozone at a low temperature gives rise to acetic and oxalic acids, alcohol, and ethyl diketobutyrate. The course of the reaction is explained by assuming that ozonisation occurs at only one double bond, and that the product then suffers fission. The reaction is studied quantitatively by estimating the

oxalic acid produced in the form of calcium oxalate. Fission of the semi-enol by means of ozone occurs in a similar manner, and gives rise to the same products. On the basis of these observations, it is possible to investigate the equilibrium of ethyl diacetylsuccinate dissolved in hexane, carbon tetrachloride, or ether. The proportion of $\alpha_1\beta$-ester is determined by the bromine titration method; the colorimetric estimation with ferric chloride gives the sum of α-ester and $\alpha_2\beta$-ester, whereas the fission by ozone gives the sum of all the enols (each of which gives a molecular proportion of oxalic acid). The examples which are cited show that chemical methods in these instances lead to results which cannot be obtained by physical means. The relative proportions of the three enols can be estimated with sufficient exactitude, but there is no process available for estimating directly the proportion of the ketonic form.

Starting from the β-ester, numerous investigations of the equilibria of diacetylsuccinic ester in various solvents have been made. The main difficulty in establishing an exact relationship between the velocity of transformation and the proportion of the enol consists in obtaining absolutely pure solvents free from catalytically active substances. It is, however, certain that equilibrium is established most rapidly, and that the keto-forms predominate in liquids of high dissociating power. Thus in the presence of water the β-variety is remarkably favoured, and all the isomerides are converted into it on contact with water. In nitromethane ($e=39{\cdot}4$), a small proportion of the $\alpha_1\beta$-ester (4·0%), but no other enol, is present. In the series of the alcohols, the $\alpha_2\beta$-ester is capable of existence; in addition, the $\alpha_1\beta$-compound is present to a considerable extent (42% in ethyl alcohol). In solvents of smaller dissociating power, such as hexane, the relationships are displaced greatly towards the other side. The β-ester is not present in appreciable amount, and the small percentage of ketonic form exists as the γ-ester. The proportion of $\alpha_1\beta$-ester recedes, whereas that of the $\alpha_2\beta$-compound attains 50%, and the dienolic form is capable of existence. The slight dissociating power of hexane, carbon tetrachloride, and ether influences markedly the rate of transformation of the isomerides. Loss of the enolic hydrogen atom which takes place instantaneously from the dienol, rapidly from the semi-enols in the presence of solvents of higher dielectric constant, becomes so retarded that even the very strongly acidic, dienolic variety is preserved. The primary formation of the $\alpha_1\beta$-ester in the establishment of all equilibria is very distinct. H. W.

Equilibrium in the System Calcium Oxalate–Dilute Hydrochloric Acid. E. CARRIÈRE and M. AUMÉRAS (*Compt. rend.*, 1923, **177**, 1288—1290).—The equilibrium in the system calcium oxalate–dilute hydrochloric acid has been studied by observing the disappearance of the calcium oxalate precipitate at a certain concentration of acid. Four influences are studied: (1) that of concentration of oxalic acid produced: by plotting concentrations of hydrochloric acid against those of oxalic acid, an almost straight line is obtained; (2) that of temperature: the concentration of

hydrochloric acid is, roughly, proportional to the solubility product of calcium oxalate at different temperatures; (3) that of excess of calcium chloride: the concentrations of hydrochloric acid are approximately proportional to the square root of the concentrations of calcium chloride; (4) that of excess of oxalic acid: the concentrations of hydrochloric acid are roughly proportional to the square root of the concentrations of oxalic acid. E. E. T.

The Catalytic Bromination of Aliphatic Acid Chlorides. W. F. GOEBEL (*J. Amer. Chem. Soc.*, 1923, **45**, 2770—2771).—α-Bromoanhydrocamphoronyl chloride (Bredt, A., 1895, i, 242) is prepared as follows. Anhydrocamphoronic acid is warmed with phosphorus pentachloride until the reaction ceases, a small quantity of iron powder is then added, and, while the mixture is heated on the water-bath, bromine is slowly added; the heating is then continued for forty-five minutes, and the mixture allowed to cool. The crude product (yield 75%) is purified by washing with dry ether and then recrystallising from benzene. W. S. N.

The Supposed Autoxidation of Cysteine. O. WARBURG and S. SAKUMA (*Pflüger's Archiv*, 1923, **200**, 203—206; from *Chem. Zentr.*, 1923, iii, 1290; cf. A., 1923, i, 11).—The autoxidation of cysteine described by Abderhalden and Wertheimer consists in reality of the oxidation and reduction of a metallic cysteine compound. G. W. R.

The Oxidation of Hydrocarbons with Special Reference to the Production of Formaldehyde. V. The Slow Oxidation of the Higher Liquid, Saturated Hydrocarbons. T. S. WHEELER and E. W. BLAIR (*J. Soc. Chem. Ind.*, 1923, **42**, 491—497T).—Experiments on the oxidation of hexane were made, using a method previously described (A., 1923, i, 1175), in which the hydrocarbon mixed with oxygen is passed through a hot tube. The temperatures used were 480°, 520°, 540°, and 590°, the time of heating being 2 sec. The products obtained included higher aldehydes, unsaturated hydrocarbons, formaldehyde, acids in small quantity, carbon monoxide, carbon dioxide, hydrogen at higher temperatures, and water. In presence of excess of oxygen, much of the hexane consumed appears as higher aldehydes, just as with other hydrocarbons, except methane (cf. T., 1923, **123**, 2079). The amount of carbon dioxide formed also increases when more oxygen is used, and as the rate of oxidation of the hexane does not increase as fast as would be expected from the law of mass action, it is clear that surface action is predominant. As the temperature increases, less of the higher aldehyde appears in the product, but more formaldehyde, unsaturated hydrocarbon, carbon monoxide, and carbon dioxide. The unsaturated hydrocarbon at all temperatures is mainly ethylene and the higher aldehydes tend towards acetaldehyde with increasing temperature. No saturated hydrocarbons appear in the products, showing that thermal decomposition of the hexane does not occur appreciably, otherwise methane would appear in quantity. The results are discussed in connexion

with those obtained by other workers, and the probable course of the slow oxidation of hydrocarbons generally is shown diagrammatically. E. H. R.

Condensation of Aldehydes to Esters by Aluminium Ethoxide. W. C. CHILD and H. ADKINS (*J. Amer. Chem. Soc.*, 1923, **45**, 3013—3023).—During an investigation on the condensation of acetaldehyde to ethyl acetate, using aluminium ethoxide as catalyst, it was found that the latter existed in two forms. When prepared by the method of Wislicenus, the α-form only was produced, and this solidified at a little above the ordinary temperature; it was partly converted into the β-form, m. p. 140°, on distillation. The β- was completely converted into the α-form by heating in a sealed tube at 275° for fifteen hours. Both forms had the same catalytic activity, being more active than Henle's ethoxide (A., 1920, ii, 446). The presence of water in the catalyst or in the aldehyde was detrimental. The effect of the addition of a third substance on the rate of reaction was studied, and the results show that alcohols containing fewer than six carbon atoms are inhibitors, methyl alcohol being the most effective, whilst the chlorides of aluminium, mercury, calcium, and zinc are promoters. The addition of increasing amounts of aluminium chloride was accompanied by increasing yield of ethyl acetate to a certain value; further increase in the amount of promoter caused a decreased production of ester and an increase in the rate of paracetaldehyde formation. The reaction apparently takes place in a homogeneous system and the exclusion of light has no effect. The temperature coefficient of the reaction in xylene solution is approximately 1·30 for a rise of 10° in the vicinity of the ordinary temperature.

F. B.

The Activation of Hydrogen in Organic Compounds. E. H. USHERWOOD (*Chemistry and Industry*, 1923, **42**, 1246—1251).—The presence of activated hydrogen in an organic compound may be recognised by a number of properties, among which may be mentioned diad or triad tautomerism, ability to form metallic derivatives, and capacity for alkylation. The ability of a compound to take part in an aldol reaction, a Michael reaction $[H]—C< + >C=C< \rightarrow [H]—C—C—C<$ or a Thorpe reaction $[H]—C< + N\equiv C— \rightarrow [H]—N=C—C<$ may also be taken as evidence of the presence of an activated hydrogen atom, indicated above in square brackets. The phenomenon of tautomerism may be regarded as due to the migration of an activated hydrogen atom within the molecule thus: $>C[H]—C=O \rightleftharpoons >C=CO[H]$. There is a strong formal resemblance between this reaction and the aldol reaction $>C[H]X + >C:O \rightleftharpoons >CX—C—O[H]$, and this resemblance is intensified by a recent demonstration that the aldol reaction is reversible. Keto-enol tautomerism may therefore be

regarded as an intramolecular aldol reaction. There is a similar analogy between three-carbon tautomerism and the Michael reaction. The structural conditions necessary for the activation of a hydrogen atom to give rise to the above phenomena may be provisionally embraced in two formulæ: (1) The hydrogen atom represented by [H] in the group [H]C≡X is activated no matter whether X is C or N; (2) The hydrogen atom in the group [H]C—X=Y or [H]≡C—XY is activated no matter whether X is C or N, provided Y is either the electronegative O, N, or S, or is C, which itself is involved in the group =C—X=Y or =C—X≡Y. The benzene nucleus, considered as a Kekulé individual, forms a special case of the second rule, and it enters into a number of reactions which show that it possesses an activated hydrogen atom. A number of such reactions are discussed, including the addition of benzene to cinnamic acid, the conversion of β-imino-γ-cyano-α-phenylpropane into 1 : 3-naphthalenediamine, and Skraup's quinoline synthesis.

E. H. R.

Production of Acetone by the Action of Potassium Acetate on Acetic Anhydride. E. Luce (*Compt. rend.*, 1923, **177**, 1306—1309).—When an equimolecular mixture of potassium acetate, acetic acid, and acetic anhydride is heated under reflux for thirty hours in a bath kept at 170—180°, some acetone and carbon dioxide are formed. Equimolecular mixtures of potassium acetate and acetic acid, or of acetic anhydride and acetic acid, when similarly treated, give practically no acetone. An equimolecular mixture of potassium acetate (100 g.) and acetic anhydride, however, gives 12·32 g. of carbon dioxide, corresponding with a considerable production of acetone, most of which is lost by polymerisation or evaporation. If the acetone is allowed to distil as fast as it is formed, about 24% of the theoretical quantity (see below) is obtained.

This type of reaction was observed first by Perkin (T., 1886, **49**, 317), whose explanation has now been confirmed. Thus, when a mixture of potassium butyrate and acetic anhydride interacts, acetone and methyl propyl ketone are formed, as would be expected from the decomposition of the intermediate compound,

$$OK\cdot CPr^{\alpha}(OAc)_2,$$

whereas, if the reaction were due simply to the decomposition of the acid anhydride, acetone alone would result, whilst interaction (with elimination of potassium carbonate) of 2 mols. of alkali salt would only lead to the formation of dipropyl ketone. E. E. T.

Ketenic Decomposition of Ketones. Keten and Methylketen. C. D. Hurd (*J. Amer. Chem. Soc.*, 1923, **45**, 3095—3101; cf. A., 1911, i, 307).—Acetone vapour was decomposed by contact with a hot platinum wire filament, but the yield of keten was not so good as in the method previously described (A., 1923, i, 1060). Both methyl ethyl ketone and diethyl ketone gave a mixture of methylketen and keten. The presence of keten in the product from diethyl ketone must be due to the decomposition of methylketen. F. B.

Oxidation of Carbohydrates. J. STIEGLITZ (*Proc. Inst. Med. Chicago*, 1916—1917, **1**, 41—50).—In the oxidation of dextrose, an intra-atomic phenomenon involving the loss of electrons by the carbon atoms, and essentially like that of an element, the production of an electric current has been observed. The presence of alkalis causes great acceleration, and of acids, retardation; the former condition yields decomposition products more readily oxidised than dextrose itself. There is evidently some fundamental specific factor, probably the oxidising enzymes, having a paramount influence on the physiological processes of oxidation of carbohydrates. CHEMICAL ABSTRACTS.

Sources of the Rare Sugars. XI. Preparation of Mannose. XII. Preparation of Inulin. T. SWANN HARDING (*Sugar*, 1923, 583—585, 636—638).—*Mannose.*—A modification of the method of Hudson and Sawyer (A., 1917, i, 321) is described: Ivory sawdust is mixed with its own weight of sulphuric acid (75%), hydrolysed as directed by Hudson and Sawyer (*loc. cit.*), and barium carbonate added until the reaction is neutral to Congo-red paper. After adding sufficient phosphoric acid to impart a slight acidity, using the same indicator, and also some decolorising carbon, the liquid is filtered. Basic lead acetate is added to the filtrate, which is concentrated to a thin syrup in a vacuum, and treated with twice its volume of alcohol. After further concentration, and the addition of a little glacial acetic acid, crystallisation is readily effected, the mass obtained being diluted with alcohol containing 1% of nitric acid, and the sugar filtered and washed with the acid–alcohol on a Buchner funnel. Lastly, it is dried in a vacuum at the ordinary temperature, ground finely, and the drying continued for twenty-four hours while gradually raising the temperature to 46°, mannose free from acetic acid thus being obtained.

Inulin.—A mixture of 1,000 g. of finely ground chicory root and 5 litres of water is boiled for one hour, filtered, and the residue washed with hot water. The filtrate and washings are treated at 40° with basic lead acetate, using a slight excess over that required for the precipitation of the impurities, decolorising carbon is added, the excess of lead thrown down with hydrogen sulphide, and the liquid filtered. After concentrating the filtrate to about 500 c.c., and adding twice its volume of 80% alcohol, the mixture is allowed to remain over-night, when 10—15 per cent. of inulin will deposit. This is dissolved in 1,000 c.c. of 40% alcohol, treated with decolorising carbon, and filtered. Two volumes of 80% alcohol containing 1% of nitric acid are added, the liquid is left over-night at a low temperature, and the inulin obtained dried in a vacuum at about 35° and reprecipitated. J. P. O.

Solubility and Insolubility of Starch. G. MALFITANO and M. CATOIRE (*Compt. rend.*, 1923, **177**, 1309—1311).—A 1% aqueous solution of potato starch was obtained (heating not above 80°), the cooled product, consisting of two layers, then being diluted to one-tenth of its original concentration, and the clear portion

evaporated. The gelatinous starch separating did not give a clear solution with boiling water, and on being dried merely swelled when so treated. After washing with water and then with alcohol, the product (containing, like the original material, combined phosphorus, calcium, magnesium, and silicon) resembled cotton, dissolving in water only when heated at 150° with the latter, and being reprecipitated on cooling. On treatment with acids, etc., it gave a product resembling soluble starch.

It is concluded that the solubility of starch depends on the inorganic matter present, starch itself being amylaceous matter combined with phosphates and silicates (of calcium and magnesium).

E. E. T.

Starch Paste. I. Relation between the Viscosity of Wheat Starch Paste and the Concentration and Temperature. MORIZO YOSHINO (*J. Chem. Ind. Japan*, 1923, **26**, 870—873).—The viscosity was measured by Ostwald's capillary viscosimeter at 20°, 30°, 40°, and 50° for the range of concentration of 0·5—2·5%. The relation between viscosity and concentration is expressed with sufficient accuracy by Arrhenius's formula, $\log \eta/\eta_0 = \theta C$, where $C = 100p/[100-(n+1)p]$, p being the number of grams of starch in 100 grams of paste and n the hydration factor. The amount of water absorbed decreases according to the elevation of temperature. The values of θ and n were observed to be as follows: 0·412 and 12·6 at 20°, 0·407 and 10·0 at 30°, 0·407 and 7·6 at 40°, and 0·408 and 5·7 at 50°. When the values of p become 7·4 at 20°, 9·1 at 30°, 11·6 at 40°, and 14·9 at 50°, the viscosity becomes infinite; that is, the solution changes into a solid. K. K.

Cellulose. VIII. K. HESS, W. WELTZIEN, and E. MESSMER (*Annalen*, 1923, **435**, 1—144).—(*A*) *Cuprammonium-cellulose solutions*, E. MESSMER [and, in part, (FRL.) ELLY JAGLA].—It has already been shown (A., 1921, i, 401) that the copper is present in cellulose–cuprammonium solutions as an optically active complex anion and as (kation) an ammine. The solutions have now been examined further from a mass-action point of view, and the molecular complexity of the dissolved cellulose has been determined. In order to make such a determination trustworthy, the following points had to be proved: (1) Cellulose (in cuprammonium solutions) undergoes no hydrolytic decomposition. This is clearly the case, since the maximum rotation, for a particular concentration, is reached immediately dissolution of cellulose is effected. (2) The rotation is due to a single complex copper compound of high rotatory power. This is shown by the form of the rotation curves (concentration of components of solution against rotation, etc.). Moreover, a maximum rotation is observed when the solution contains 1 atom of copper to 1 mol. $C_6H_{10}O_5$. (3) The copper complex is in equilibrium with very weakly rotating cellulose (the latter functioning, in dissolving, as a base). This is shown by other curves, connecting rotation and concentration of copper. A slight excess (1 mol.) of copper is necessary to drive back the dissociation of the complex. When excess of copper is present, addition of

cellulose, within limits, causes a rectilinear rotation-increase curve. (4) The (reacting) copper is used entirely to give the strongly rotating complex. This is shown by studying the effect of sodium hydroxide, which does not increase the rotatory power of the solution (see equation 2 below). (5) The copper dissolves unimolecularly. This is shown by a parallel investigation of dextrosemonoacetone (below).

The above relations are expressed by the equation: mCu+$n(C_6H_{10}O_5)_x \rightleftharpoons$ Cellulose-copper Complex, and since it has been shown (2, above) that an atom of copper corresponds with $C_6H_{10}O_5$, in the given solution, $m=nx$.

The formation of a cellulose–cuprammonium solution is expressed by the following equations: (1) In absence of alkali, cellulose is dissolved by cuprammonium hydroxide: (*a*) $(C_6H_{10}O_5)_x$(solid)+$[Cu(NH_3)_4](OH)_2 \longrightarrow 2H_2O+[C_6H_9O_5]_2[Cu(NH_3)_4]$; (*b*) (giving the complex of high rotatory power): $[C_6H_9O_5]_2[Cu(NH_3)_4]+2[Cu(NH_3)_4](OH)_2 \rightleftharpoons [C_6H_7O_5Cu]_2[Cu(NH_3)_4]+8NH_3+4H_2O$. (2) In presence of alkali (which takes the place of cuprammonium hydroxide): $Na[C_6H_9O_5]+[Cu(NH_3)_4](OH)_2 \rightleftharpoons [C_6H_7O_5Cu]Na+4NH_3+2H_2O$. The equations (1) and (2) may be summarised thus: $[C_6H_9O_5]'+[Cu(NH_3)_4]''+2OH' \rightleftharpoons [C_6H_7O_5Cu]'+4NH_3+2H_2O$. (3) In presence of excess of alkali: $[C_6H_9O_5]Na+[C_6H_7O_5Cu]Na \longrightarrow \left[\begin{matrix}C_6H_9O_5\\C_6H_7O_5\end{matrix}Cu\right]Na_2$ (the last formula relating to the copper–sodium–cellulose complex precipitated in presence of excess of alkali).

Since in equation (1) above, the copper has two functions, the investigation of this solution will throw little light on the question at issue. In presence of alkali (2), however, the copper has only one function. If α=rotatory power of the copper complex, a and b are, respectively, the total number of copper atoms and $C_6H_{10}O_5$ units present in volume v, and x is the number of $C_6H_{10}O_5$ units in the combined cellulose, then, for the interaction of m atoms of copper and n molecules of cellulose, K, the reaction constant, is given by $K=(a/v-m\,.\,\alpha\,.\,k)^m(b/xv-n\alpha k)^n/\alpha\,.\,k$. Various values (1 to 4) were taken for m, n, and x, and k and K determined, whence, knowing α and b, a could be calculated. Approximate agreement between a (found) and a (calc.) was only obtained for (1) $n=m=x=1$, (2) $n=m=1$, $x=2$, (3) $n=2$, $m=3$, $x=1$, and (4), $n=3$, $m=4$, $x=1$. Of these possibilities, (2), (3), and (4) are excluded on other (experimental) grounds, as is also the possibility of expressing (1) as $n=m=x=2$ (*i.e.*, 2Cu : $C_{12}H_{20}O_{10}$ —*i.e.*, cellobiose) or as $n=m=x=3$, and so on.

From the above, it follows that in cuprammonium solutions of cellulose (say, one containing 28 mols. of cellulose, 15 mols. of copper, and 25 mols. of sodium hydroxide), cellulose reacts as if it possessed the molecular formula, $C_6H_{10}O_5$. The correctness of this conclusion was established in other ways. Thus, solutions containing x mols. of cupric hydroxide and y mols. of cellulose gave the same rotation as solutions containing y mols. of cupric hydroxide and x mols. of cellulose.

Experiments were also carried out (cf. A., 1921, i, 401) with cuprammonium solutions of other carbohydrates or their derivatives. Cellobiose had $[\alpha]_{435\cdot8}$ +50·6°, +50·6°, and +160·0° in aqueous, in ammoniacal sodium hydroxide, and in sodium hydroxide–cuprammonium solutions, respectively. The investigation of the solutions is rendered difficult because of mutarotation, oxidation, etc. α-Methylglucoside, in the above three solvents, had $[\alpha]_{435\cdot8}$ +324°, +340°, and +460°. The tendency of the glucoside to form copper complexes is very strong. Although, for this reason, the equilibrium relationship could not be experimentally investigated, clear evidence was obtained that the increased rotation of the cuprammonium solutions was due to a complex, 1 glucoside : 1 copper. β-Methylglucoside, in the above three solvents, had $[\alpha]_{435\cdot8}$ −57·4°, −53·3°, and +38·1°, respectively. The quantitative study of the cuprammonium solutions of the last three compounds is complicated by the rotation possessed by these compounds. In the case of dextrose mono*iso*propylidene ether, which had, in the above three solvents, $[\alpha]_{435\cdot8}$ −24·8°, −31·6°, and −212·5°, respectively, the equilibrium was amenable to experiment, and the existence of the complex, containing 1Cu : $C_9H_{16}O_6$, definitely established. Moreover, the molecular weight of the dissolved dextrose mono*iso*propylidene ether was determined as in the case of cellulose, and also by direct cryoscopic measurement in aqueous solution, when a normal result was obtained. Dextrose monopropylidene ether was found to have m. p. 160·5—161°, $[\alpha]_D^{15}$ −12·12° (cf. Fischer and Rund, A., 1916, i, 363).

Lævoglucosan gives no complex in cuprammonium solutions, the rotation in the latter being the same as that of an aqueous solution.

(*B*) *The acetylation of cellulose* (W. Weltzien [and, in part, R. Singer, H. Jensen, and A. Reh]).—Whilst dried cotton cellulose does not react with pure, dry, acetyl chloride, cotton cellulose containing 4—5% of moisture, when shaken for four days with eleven times its weight of acetyl chloride at 17—20°, is converted (92% yield) into crude cellulose triacetate *A*. If the cooled solution obtained is allowed slowly to lose the hydrogen chloride present, evaporated in a vacuum, the residue treated with chloroform, and the latter evaporated, a solution of the second residue in glacial acetic acid then being precipitated with ether, pure *cellulose triacetate A* is obtained as a pale yellow or colourless powder (60% yield).

If in the original acetylation the conditions are varied, by-products (formed in the above preparation in small quantities), viz., *cellodextrin acetate* and acetochlorocellobiose, are obtained in larger quantities, although they are readily separable from cellulose triacetate *A*. The acetylated celluloses described by Skraup (A., 1906, i, 67) and by Zechmeister (A., 1923, i, 306) are mixtures. (In connexion with the analysis of cellulose acetates, a modification of the Ost and Katayama and the Wenzel method is described, steam vacuum distillation being used. A diagram of the apparatus used is given.)

Cellulose triacetate *A* has m. p. 270—275° (decomp., with brown coloration and frothing), is soluble in chloroform and acetic acid, and insoluble in alcohol or ether. Dissolution is preceded by swelling. Cellulose triacetate *A* has $[\alpha]_D$ −16·7° in chloroform and +4·40° in glacial acetic acid. Its solutions in the latter solvent throw little light on its molecular weight, a constant depression being obtained for all solutions containing between 0·03 and 0·3% of the acetate, whilst irregular results are obtained with higher concentrations. The constant depression obtained with low concentrations may be due to the presence of water (cf. Paternò and Salimei, A., 1913, ii, 849). In phenol, cellulose triacetate *A* gives a mol. weight value of 2,380—3,350 (with a specimen obtained in a slightly different manner, 2,030—2,270). Ost's cellulose acetate (in phenol) had a variable mol. weight (2,037—10,133). On treatment with a mixture of acetic and sulphuric acids, Ost's cellulose acetate became more like cellulose triacetate *A*. Thus, whilst originally its product of alkaline hydrolysis was practically insoluble in alkali, after the acetic–sulphuric acid treatment, the hydrolysis product was soluble in alkali.

Cellulose triacetate *A*, on treatment with cold *N*-methyl-alcoholic sodium hydroxide, affords *cellulose A*, readily soluble in 2*N*-sodium hydroxide, the solution affording cellulose *A* on acidification. Cellulose *A* is a white powder with $[\alpha]_D$ (in 2*N*-NaOH) −12·4°. It is shown by *X*-ray analysis to be crystalline, whilst its rotatory power in cuprammonium solutions establishes clearly its structural identity with the original cotton cellulose used. An alkaline solution of cellulose slowly undergoes hydrolysis, reducing properties developing. In the methyl-alcoholic alkaline hydrolysis (above), a little of the reducing substances is formed, and is removed by treating the alkaline solution with ammonia, when pure cellulose *A* is precipitated. In this connexion, it is found that the Schwalbe copper number does not always give trustworthy comparisons of reducing power. A method based on the precipitation of the cellulose to be tested as the sodium–copper derivative (above) is described. Pure cellulose *A* and hydrocellulose (as prepared by Knoevenagel and Busch, A., 1922, i, 636) show no reduction with the improved method, the crude products showing feeble reduction. Ost's cellulose acetate, after acid treatment (as above) was feebly reducing, whilst cellodextrin acetate, and the acetyl derivative obtained by treating cellulose with acetyl chloride at 24—27° were strongly reducing.

By effecting the acetylation of cellulose with acetyl chloride, in presence of acetic anhydride, which decreases the concentration of hydrogen chloride ($Ac_2O + HCl \rightleftharpoons Ac\cdot Cl + Ac\cdot OH$), a cellulose acetate was obtained which, on hydrolysis, gave a cellulose less soluble in alkali than cellulose *A*.

Cellodextrin acetate is a white, amorphous powder, m. p. 260° (softening at 250°), $[\alpha]_D^{18}$ −11·0 (±2·0)°, $[\alpha]_D^{17\cdot5}$ −12·0 (±1·5)°, in chloroform. It is more soluble in solvents than is cellulose triacetate *A*. It gives a molecular weight in acetic acid of 318—1,366, in phenol of 1,260—1,480, in urethane of 1,500—1,540, and

in naphthalene of 1,350—1,470. On hydrolysis with methyl-alcoholic sodium hydroxide, it gives *dextrin* as a white powder, which darkens without melting, reduces Fehling's solution under proper conditions (above), and is converted by acetyl bromide containing hydrogen bromide into acetobromocellobiose, whilst acetic anhydride (and a trace of sulphuric acid) converts the dextrin into octa-acetylcellobiose (m. p. 228°).

(*C*) *Methylation of Cellulose A* [W. WELTZIEN.]—The methylation of cellulose, as effected in presence of alkali (Irvine, T., 1923, **123**, 518), gives results of doubtful value, owing to the definite action of alkali on cellulose at the temperature of methylation. Cellulose *A*, on warming with dilute alkali, is so altered that it reduces Fehling's solution, and is no longer precipitated on acidification. Hydrated barium hydroxide has no effect on cellulose *A*, and methylation carried out using this hydroxide and methyl sulphate (at 90—95°) may be assumed to proceed without effecting structural changes. The product obtained in this way was a yellow glass (OMe=30—40%), insoluble in, and unaffected by, alkali, and on further methylation with sodium hydroxide and methyl sulphate (at 80—90°) for three hours gave a product (OMe=42—43%) corresponding with trimethyl cellulose *A*. Further methylation (using silver oxide and methyl iodide or piperidine and methyl sulphate) was impossible. *Trimethyl cellulose A* is a white powder, m. p. 230—245° (softening at 217°), dissolving in cold water and separating on heating this solution, owing to hydrate formation, etc. It has $[\alpha]_D^{10}$ −18° in water and is inactive in chloroform solution. The freezing-point depression of an aqueous solution slowly decreased on keeping, a result in accordance with the structural similarity of trimethyl cellulose *A* to cellulose *A*. It is concluded that the results obtained by Heuser and von Neuenstein (A., 1923, i, 17) indicate that these authors were dealing with a partly hydrolysed cellulose complex.

(*D*) *Action of Hydrogen Bromide on Cellulose triacetate A* [K. HESS, W. WELTZIEN, and F. KUNAU.]—Cellulose triacetate *A*, when treated in glacial acetic acid solution with hydrogen bromide, gave acetobromocellobiose (yield, 10—30%). No hexa-acetylbromocellobiose but a little hepta-acetylbromocellobiose was also formed.

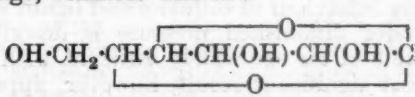
Cellulose triacetate *A* is unaffected by acetyl bromide, but, in presence of hydrogen bromide, a 50% conversion into acetobromocellobiose results. There is also formed a new *acetobromodextrose* (white, amorphous powder, m. p. 60—70° [indef.], $[\alpha]_D$ +80°) which does not yield penta-acetyldextrose when treated with silver acetate. The new compound does not depress the freezing point of bromoform, has a normal molecular weight in acetic acid and in phenol, and is (twice) associated in benzene solution. It affords acetobromocellobiose when treated with acetyl bromide containing hydrogen bromide. The acetobromodextrose is readily deacetylated by the method of Fischer and Bergmann (A., 1919, i, 278), whereas acid hydrolysis caused the elimination of bromine, with formation, in very variable yield, of a new substance, *cellogluconsan*, $C_6H_{10}O_5,H_2O$, plates, m. p. 107—109°, $[\alpha]_D$ +89·31°, in

aqueous solution. The molecule of water is firmly attached, and the substance (which is accompanied in its formation by a bromine-free amorphous substance) is not hygroscopic, like some glucosans (below). *Tribenzoylcelloglucosan* has m. p. 126—128°. Celloglucosan is unaffected by boiling alkali, but affords reducing compounds on acid hydrolysis. It is quantitatively converted by methyl alcohol containing a trace of hydrogen chloride into α-methylglucoside, a fact which is difficult to reconcile with Karrer's suggestion that cellulose is derived from β-glucose (A., 1920, i, 370). Celloglucosan in many respects resembles glucosan (Pictet and Castan, A., 1920, i, 594), but, unlike the latter substance, does not reduce Fehling's solution. The rotation of an aqueous solution of celloglucosan is higher than that of a similar solution of glucosan, but falls to the rotation of the latter if a little hydrochloric acid is added.

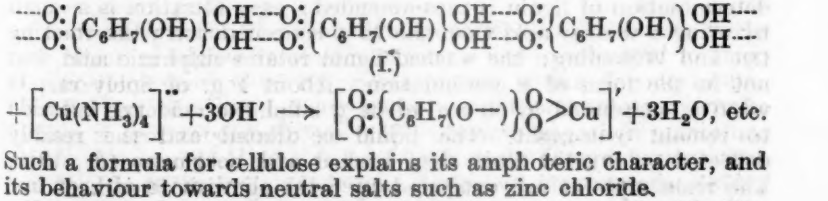
The formation of the new acetobromodextrose, which cannot, like its previously known isomeride, be obtained from cellobiose, proves that cellulose may be converted into derivatives of dextrose without the intermediate formation of cellobiose.

It is concluded (in a comprehensive survey of the whole of the work) that natural (cotton) cellulose is built up from glucose anhydride units, which are associated, not condensed or polymerised. The *X*-ray diagrams of natural cellulose, and of the cellulose (shown to be a chemical individual) obtained by precipitating cuprammonium solutions, suggest, but do not prove, the identity of these two products. Cellulose and cellulose *A* give identical values for *k* and *K* when examined by the above (cuprammonium) method, whilst the hydrolysis product of Ost's cellulose acetate is also shown to be identical, from the same point of view, with cellulose.

If 2 : 3 : 6-trimethylglucose is produced (Irvine, *loc. cit.*) without structural change, cellulose will be :



At variance with this formula, however, are the results of the action of hydrogen bromide on cellulose triacetate *A*. The authors prefer to write cellulose as I in the scheme below, when its dissolution in cuprammonium solution (which effects saturation of the partial valencies involved in the association of the simple cellulose units) is expressed thus :



(I.)

Such a formula for cellulose explains its amphoteric character, and its behaviour towards neutral salts such as zinc chloride.

An interesting, but probably misleading, fact is the identity of the heats of combustion of cellulose and of lævoglucosan.

Natural cellulose may contain as its crystal unit (cf. *X*-ray analysis) four $C_6H_{10}O_5$ residues associated together.

An important result also emerges: cellobiose need no longer be regarded as a degradation product of cellulose, the converse being nearer the truth. E. E. T.

Comparative Investigations of Cellulose and Lignin. F. Fischer and H. Tropsch (*Ber.*, 1923, **56**, [*B*], 2418—2428).—A restatement and extension of the work carried out in the authors' laboratory during recent years.

The hydrogenation of cellulose and lignin by hydriodic acid under pressure does not appear to be suitable to the elucidation of the genetic relationships between the substances, since the course of the change is not obvious and has led to very conflicting results in the hands of various workers.

Cellulose is far more stable than lignin towards aqueous alkali hydroxide under pressure and at elevated temperatures. It is completely dissolved at 300° with production of much carbon dioxide. Lignin, on the other hand, is decomposed by 9·5*N*-potassium hydroxide solution at 300° with production of phenols or phenolcarboxylic acids and adipic acid, and by 10*N* sodium hydroxide solution at 250° with formation of succinic and oxalic acids. Lignin easily becomes autoxidised in the presence of sodium hydroxide, yielding humic acids, non-volatile acids such as succinic, oxalic, and (?) *iso*phthalic, in addition to acetic, formic, and carbonic acids; cellulose is comparatively little attacked. Similar differences are observed in the oxidation of the substances under pressure; it is significant that whereas cellulose yields aliphatic acids, aromatic acids are, in addition, obtained from lignin. The ready nitration of lignin by 5*N* nitric acid is in harmony with a phenolic structure.

The comparative behaviour of cellulose and lignin when subjected to distillation under diminished pressure is described in detail. The yields of coke and tar are widely different with the two compounds. The most significant result, however, appears to be the absence of optically active compounds in the aqueous extracts of lignin tar, whereas under like conditions lævoglucosan is obtained from cellulose. It appears therefore improbable that the lignin molecule is composed of polysaccharide components. H. W.

Lignin-content of Spruce Wood. P. Klason (*Cellulosechemie*, 1923, **4**, 81—84).—The sulphuric acid method for the determination of lignin is recommended; easy filtration is secured by using a weaker acid than the 72% concentration prescribed by Ost and Wilkening; the washed lignin retains sulphuric acid, but not in the form of a combination. About 1 g. of finely rasped wood is suspended in 50 c.c. of 64% sulphuric acid and allowed to remain over-night. The liquid is diluted and the residue collected on a tared filter, then washed with cold or warm water. The resin and fat are extracted by washing with 50 c.c. of hot alcohol and the lignin is then neutralised with water containing 5 c.c. of *N*/10-potassium hydroxide, washed and dried at 105°.

The correction for ash includes any sulphuric acid not removed in the washing. Calculated on dry substance the values for an eighty-year old spruce stem were: lignin corrected for sulphate, 29·4%; sulphuric acid, 3·6%; resin and fat, 1·1%. The lignin showed on analysis C, 63·97%; H, 5·32%; pentosans, 1·7%. Another stem from the same forest but of one hundred years' growth yielded only 26·6% of lignin. Deposits of "red wood" in the branches contained locally up to 37·1% of lignin. For the direct extraction of fat and resin from wood, ether appears to be the best solvent, free from drawbacks which accompany the use of benzene or alcohol. The benzene extracts always show reactions of lignin, and the alcohol extract, which is indefinite in quantity increasing with the time of extraction, contains very substantial quantities of lignin and carbohydrates in about equal proportions. As a rapid and approximate method for the determination of resin and fat, the washing of the lignin residue after treatment with sulphuric acid may be considered to be satisfactory. J. F. B.

Chloro-bismuthates. A. GUTBIER and MANFRED MÜLLER (*Z. anorg. Chem.*, 1923, **128**, 137—152).—By treatment of one molecular proportion of bismuth trichloride with three molecular proportions of the hydrochlorides of organic bases in presence of hydrochloric acid, three new series of compounds have been prepared, viz., *μ-dichloro-octachloro-dibismuthates*, $[NHR_3]_4[BiCl_5]_2$, of which the dimethylanilinium and diethylanilinium salts are described, *μ-trichloro-hexachloro-dibismuthates*, $[NH_3R]_3[Bi_2Cl_9]$, of which the methylammonium, tetramethylammonium, triethylammonium, tetraethylammonium, *n*-propylammonium, tripropylammonium, *n*-butylammonium, *iso*butylammonium, and *iso*amylammonium salts are described, and *hexachloro-bismuthates*, $[RNH_3]_3[BiCl_6]$, of which the dimethyl-, trimethyl-, ethyl-, diethyl-, *iso*propyl-, di*iso*propyl-, and allyl-ammonium salts, the methyl-, ethyl- and *iso*amylanilinium salts, and the guanidinium, pyridinium, α-picolinium, β-picolinium, lutidinium, collidinium, quinolinium, and *iso*quinolinium salts are described. The first and second series may be regarded as hexa-co-ordination compounds by assuming the formulæ given, the two bismuth atoms being linked through two and three chlorine atoms, respectively.

All the compounds are extremely sensitive to changes in environment, and decompose at once in contact with water or moist air. S. I. L.

The Derivatives of Hexachloro-antimonic Acid. A. GUTBIER and W. HAUSMANN (*Z. anorg. Chem.*, 1923, **128**, 153—168).—By combination of antimony pentachloride with alkyl- and arylamines in hydrochloric acid solution, a large number of compounds of the general formulæ $[R{\cdot}NH_3][SbCl_6]$, $[R_2NH_2][SbCl_6]$, $[R_3NH][SbCl_6]$, and $[R_4N][SbCl_6]$, as well as pyridine and piperidine derivatives, have been prepared. They are moderately stable, crystallising unchanged from hydrochloric acid in colourless, well-formed crystals; they dissolve in water to colourless solutions, which slowly become cloudy, and deposit white precipitates, but

from alcohol solution they may be recovered for the most part unchanged.

The mono-, di-, tri-, and tetra-methylammonium salts, the mono-, di-, tri-, and tetra-ethylammonium salts, the mono-, di-, and tri-propylammonium, *iso*propyl-, butyl-, *iso*butyl-, and di*iso*butyl-ammonium salts, the allyl-, *iso*amyl-, and benzyl-ammonium salts, the dibenzylethylammonium, ethylenediammonium salts, and the α-picolinium, collidinium, and piperidinium salts are described.

S. I. L.

Derivatives of Hexachloro-stannic Acid. A. Gutbier, G. Kunze, and E. Gühring (*Z. anorg. Chem.*, 1923, **128**, 169—178).—A series of alkylammonium, arylammonium, and pyridine and quinoline derivatives of the general formula $X_2[SnCl_6]$ has been prepared. They are generally colourless, and crystallise readily from hydrochloric acid solution. They dissolve readily in water, hydrolysing slowly in the cold; the freshly prepared alcoholic solutions are neutral. Tripropylammonium hexachlorostannate $[NHPr_3]_2[SnCl_6]$ crystallises in two forms, one bright rose-coloured tablets, the other deep reddish-brown leaflets.

The following compounds are described: the methyl-, dimethyl-, trimethyl-, tetramethyl, ethyl-, diethyl-, triethyl-, tetraethyl-, normal and *iso*propyl-, dipropyl-, tripropyl-, normal and *iso*butyl-, di*iso*butyl-, tri*iso*butyl-, allyl, and *iso*amyl-ammonium salts, the ethylene- and propylene-diammonium salts, and the anilinium, pyridinium, collidinium, and quinolinium salts. S. I. L.

Röntgenographic Determination of the Structural Formula of Hexamethylenetetramine. H. W. Gonell and H. Mark (*Z. physikal. Chem.*, 1923, **107**, 181—218).—The crystal structure of hexamethylenetetramine has been investigated by means of *X*-ray spectra and Laue figures. It is shown that hexamethylenetetramine does not belong to the hexakisoctahedral class, O_h, as has been assumed from macroscopic examination, but more probably it belongs to the hexakistetrahedral class T_d or possibly to the tetrahedral pentagonal dodecahedral class T. The elementary cube has an edge 7·02 Å. long and contains 2 mols. of hexamethylenetetramine. Each nitrogen atom lies between the three nearest carbon atoms in close spherical packing. The shortest distances between neighbouring atoms in the molecule are: N—C=1·48 Å. and C—C=2·58 Å. The lattice is a molecular lattice. The structure thus deduced confirms that found by Duden and Scharff (A., 1896, i, 122) from purely chemical investigation, according to which the molecule is built up of trimethylenetriamine rings. The present work furnishes an example where Röntgenographic investigation enables a decision between possible structural formulæ to be reached when such has not been possible by purely chemical treatment. J. F. S.

The Reactivity of Different Amino-acids in the Presence of Blood Charcoal, and of Hydrogen Peroxide. E. Negelein (*Biochem. Z.*, 1923, **142**, 493—505).—Measurements

have been made of the rate of oxidation in an atmosphere of oxygen, and of the adsorption constants, of various amino-acids in the presence of blood charcoal. The considerable variations found in the former, when equimolecular solutions of the various acids are brought into equilibrium with the adsorbent, are ascribed to differences in the extent of adsorption. In general, primary and secondary amino-acids are much more reactive to oxygen in the presence of charcoal than are the tertiary acids. Closely parallel results are obtained when the rates of oxidation of the amino-acids by activated oxygen (hydrogen peroxide) at p_H 9·2 are measured, the tertiary acids being again much less reactive than the others. The similarity of the two types of oxidation lends support to the views of Warburg, in which the oxidation of amino-acids in the presence of charcoal is ascribed to activated oxygen. J. P.

The Configuration of Amino-acids. II. P. KARRER (*Helv. Chim. Acta*, 1923, **6**, 957—959).—The conversion of *d*-serine into *l*-βγ-diaminopropionic acid shows that these must have the same configuration. *d*-Serine was converted into its methyl ester, which, by the action of phosphorus pentachloride, was converted into *d*-γ-chloro-β-aminopropionic acid, as described by Fischer and Raske (A., 1907, i, 900) for the corresponding *l*-compounds. The *d*-chloroaminopropionic acid was converted into *l*-diaminopropionic acid by heating with liquid ammonia. The product contained some racemate, its rotation being $[\alpha]_D^{18}$ −18·1° instead of −24·9°. It follows that *l*-serine must have the same configuration as *d*-diaminopropionic acid, which has been shown to correspond with *l*-asparagine and *l*-aspartic acid (A., 1923, i, 660). It therefore follows that the following constituents of natural albumin all have the same configuration: *d*-alanine, *l*-serine, *l*-cystine, *l*-asparagine, and *l*-aspartic acid. It would appear to be a general rule that naturally occurring amino-acids have the same configuration. E. H. R.

Aliphatic Dialkylaminoalkyl Compounds. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (U.S. Pat. 1429922; from *Chem. Zentr.*, 1923, iv, 591).—Additional data are given for compounds already mentioned (A., 1922, i, 529). Ethyl α-diethylaminoethylacetoacetate has b. p. 132—135°/10 mm., ethyl α-dimethylaminoethylacetoacetate, b. p. 124°/12 mm., ethyl diethylaminobutylacetoacetate, b. p. 138°/10 mm. G. W. R.

The Electro-chemical Preparation of Cyanuric Acid and Allophanic Esters from Formamide. K. SCHAUM [with H. SCHNEIDER] (*Ber.*, 1923, **56** [*B*], 2460—2462).—*iso*Cyanuric acid is obtained when formamide is electrolysed between platinum electrodes at a temperature not exceeding 45° with a pressure of 70 volts. A yellow substance, the nature of which has not been elucidated, is obtained as by-product; it is obtained in greater quantity if higher temperatures and current densities are employed. The electrolysis of mixtures of formamide and an alcohol leads to the formation of allophanic esters of which the methyl, ethyl, *iso*propyl, and *iso*butyl compounds have been prepared in good

yield. Apparently cyanic acid is formed intermediately either by discharge of a formamide-ion or by anodic oxidation of formamide; the former process appears to predominate when small quantities of water are present, the latter when the quantities are more considerable.

The electrolysis of molten acetamide does not give well-defined products. H. W.

Crotononitriles. A. Buelens (*Bull. Soc. chim. Belg.*, 1923, **32**, 334—337).—Crotononitrile, prepared by three different methods, dehydration of α-hydroxybutyronitrile and of β-hydroxybutyronitrile and catalytic transformation of ethyl crotonate by Mailhe's method (A., 1920, i, 476), is obtained in each case as a mixture of the two stereoisomerides, that of higher b. p. predominating. In the third case, the author shows that isomerisation occurs during catalysis as the mixture is formed in the same proportions by submitting the isomeride of higher b. p. to the conditions under which catalysis is effected. H. J. E.

The Vapour Pressure of Hydrocyanic Acid. Ryôsaburô Hara and Heima Shinozaki (*J. Chem. Ind. Japan*, 1923, **26**, 884—890).—The vapour-pressure curve of hydrocyanic acid has been determined by Smith and Menzies's static isoteniscope method (A., 1910, ii, 1036) within the range of 0—46°. It is believed that the observed values are correct to ±0·2%. The equation, $\log P_{mm} - 1836{\cdot}63/T^{1{\cdot}05} + 7{\cdot}5030$, shows satisfactory agreement with the observations. For obtaining the pressure at any desired temperatures between 0° and 47·5°, the following two values observed were used for the above formula: 519·4 mm. at 15·88° and 1128·4 mm. at 36·68°. The boiling point of the acid was found to be 25·7° instead of 26·5° as generally accepted. Considering the acid as an ideal gas, the heat of vaporisation of the acid was calculated from the Clausius–Clapeyron formula to be 246·4 cal. at 0°, 245·5 cal. at 20°, and 244·5 cal. at 45°. The results are tabulated. K. K.

Cacodyl Derivatives. F. A. Lee, C. Thing, and W. M. Dehn (*J. Amer. Chem. Soc.*, 1923, **45**, 2996—2998).—Cacodyl, prepared by Bunsen's method, is converted into the chloride, b. p. 109°, which gives the bromide, b. p. 130°, the iodide, b. p. 155—160°, and the cyanide, b. p. 138°, when heated with the molecular proportion of potassium bromide, iodide, and cyanide, respectively. Oxidation of the chloride with moist air gives hydrated cacodyl oxychloride, m. p. 85°. Cacodyl chloride reacts with mercurous and mercuric chlorides, cuprous and cupric chlorides to form additive compounds, which are described. F. B.

Aliphatic Arseno-compounds. I. Arsenoacetic Acid and Tetra-arsenoacetic Acid. C. S. Palmer (*J. Amer. Chem. Soc.*, 1923, **45**, 3023—3029).—The barium salt of arsinoacetic acid $(AsO_3Ba{\cdot}CH_2{\cdot}CO_2)_2Ba$ was quantitatively produced from chloroacetic acid by reaction with excess of sodium arsenite; the reaction mixture was acidified with acetic acid, the precipitated arsenic trioxide filtered off, and the filtrate added to a solution of barium

chloride. The barium salt was converted into the sodium salt and treatment of the latter with sulphuric acid and sodium hypophosphite gave *arsenoacetic acid*, $CO_2H{\cdot}CH_2{\cdot}As{:}As{\cdot}CH_2{\cdot}CO_2H$, yellow crystals, decomp. above 200°. Simultaneous reduction of one molecular equivalent of arsenic trioxide and two of arsinoacetic acid in the cold gave tetra-arsenoacetic acid,

$$CO_2H{\cdot}CH_2As{:}As{\cdot}As{:}As{\cdot}CH_2{\cdot}CO_2H,$$

a vermilion red, crystalline powder, decomp. at 180°. F. B.

Preparation of Arsinic Acid Derivatives of Aliphatic Carboxylic Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (Austr. Pat. 93325, and Swiss Pat. 97977; from *Chem. Zentr.*, 1923, iv, 721).—Aliphatic halogen carboxylic acids or their derivatives such as amides or esters are treated with arsenious acid, its derivatives, or its salts, in the presence of alkaline reagents. For example, from chloroacetic acid and arsenious oxide *arsinoacetic acid* is obtained as colourless crystals, m. p. 152°. Sodium arsenite and ethyl acetate give *ethyl arsinoacetate*, light yellow leaflets, m. p. about 95°. *Arsinolactic acid* is a viscous, yellow syrup obtained from β-chlorolactic acid and arsenious acid. *Di-arsinoadipic acid*, from dibromoadipic acid, forms colourless crystals, m. p. 165° (decomp.). Phenylarsine oxide and chloroacetic acid give *arsinophenylacetic* acid, m. p. 145° (decomp.). G. W. R.

Oxidation of Magnesyl [Magnesium Alkyl] Derivatives by Means of Hydrogen Peroxide. B. ODDO and R. BINAGHI (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 349—353; cf. A., 1922, i, 314).—When oxidised by means of hydrogen peroxide, magnesium *sec.*- and *tert.*-alkyl bromides yield the corresponding alcohols. Similarly, phenols are obtained from magnesium aryl bromides with the exception of magnesium phenyl bromide, and substituted hydroxylamines and per-acids from the products formed by replacing the active hydrogen of primary amines and of the carboxyl group by the grouping MgBr.

Treatment of magnesium phenyl bromide with hydrogen peroxide may give rise to the initial formation of phenol, but the products recognised are phenyl ether, *p*-hydroxyphenyl ether, benzene, diphenyl, and, possibly, phenyl peroxide.

With the other organomagnesium compounds, however, the oxidation proceeds normally and, especially with compounds of the types $R_2{:}CH{\cdot}MgBr$ and $R_3{:}C{\cdot}MgBr$, with such regularity in respect to time as to furnish fresh support to the view that only one of the oxygen atoms of hydrogen peroxide is quadrivalent and to strengthen the analogy in behaviour and constitution between the peroxide and formaldehyde (*loc. cit.*). Thus, with hydrogen peroxide, $CHR_2{\cdot}MgBr \longrightarrow CHR_2{\cdot}O(:H_2){\cdot}O{\cdot}MgBr \longrightarrow CHR_2{\cdot}[OH_2]{\cdot}OH \longrightarrow CHR_2{\cdot}OH$, and $CR_3{\cdot}MgBr \longrightarrow CR_3{\cdot}O(:H_2){\cdot}O{\cdot}MgBr \longrightarrow CR_3{\cdot}[OH_2]{\cdot}OH \longrightarrow CR_3{\cdot}OH$, and with formaldehyde, $CHR_2{\cdot}MgBr \longrightarrow CHR_2{\cdot}CH_2{\cdot}O{\cdot}MgBr \longrightarrow CHR_2{\cdot}CH_2{\cdot}OH$, and $CR_3{\cdot}MgBr \longrightarrow CR_3{\cdot}CH_2{\cdot}O{\cdot}MgBr \longrightarrow CR_3{\cdot}CH_2{\cdot}OH$.

Ethyl hydroperoxide may be regarded as having the aldehydic structure $O{:}OEt{\cdot}H$, so that, like the aldehydes, it should yield

alcohols of the three series when treated with the three types of magnesium alkyl derivatives. Ethyl peroxide, on the other hand, having the ketonic constitution, $O{:}OEt_2$, should yield always secondary and tertiary alcohols.

An outline is given of the experimental results, which are to be published elsewhere. T. H. P.

Behaviour of Mercuric Salts of Organic Acids towards Heat. M. S. KHARASCH and F. W. STAVELEY (*J. Amer. Chem. Soc.*, 1923, **45**, 2961—2972); cf. A., 1922, i, 189).—The behaviour of mercuric salts of substituted acetic acids on heating depends on the character of the substituting group. Thus mercuric αα-dimethylpropionate was not decomposed when heated in a vacuum at 240° for twenty minutes or when melted in air, whilst the mercury salts of phenylacetic, diphenylacetic, and triphenylacetic acid gave various products, but none in which the mercury replaces a hydrogen atom attached to the α-carbon atom. The ease with which the salt loses carbon dioxide is an important factor. When mercuric αα-diethylacetoacetate, m. p. 103°, is heated in a vacuum at 85° carbon dioxide is evolved and *mercury bis-α-acetyl-α-ethylpropyl*, m. p. 109°, is formed. Treatment of this compound with mercuric chloride gives *α-acetyl-α-ethylpropylmercuric chloride*, $CEt_2Ac{\cdot}HgCl$, m. p. 77°. On heating mercuric dimethylacetoacetate in a vacuum at 90°, *mercury bis-α-acetyl-α-isopropyl*, m. p. 120°, is produced. This gives a mercuric chloride compound, m. p. 124·5°. Mercuric αα-dimethylpropionate, m. p. 235°, did not give off carbon dioxide when heated at 240° in a vacuum. When benzoylacetic acid and mercuric oxide are heated in alcohol solution *mercury diphenacyl*, $Hg(CH_2{\cdot}COPh)_2$, m. p. 159·5°, is formed, and this on treatment with mercuric chloride gives *phenacylmercuric chloride*, m. p. 146°, which is identical with the substance of known constitution prepared by direct mercuration of acetophenone (A., 1902, i, 849). When benzoylacetic acid and mercuric oxide are heated in chloroform solution, the product is *anhydro-α-hydroxymercuribenzoylacetic acid*, $COPh{\cdot}CH<\begin{matrix}CO\\Hg\end{matrix}>O$, decomp. 290°. On adding a solution of mercuric acetate to a solution of phthalidecarboxylic acid, *mercuric phthalidecarboxylate*,

$$\left(CO<\begin{matrix}C_6H_4\\O\end{matrix}>CH{\cdot}CO_2\right)_2Hg,$$

is obtained. This reacts with sodium hydroxide to give phthalonic acid and phthalidecarboxylic acid, and has m. p. 195° (decomp.), forming dihydrophthalide, m. p. 250°. Benzoylformic acid in alcohol solution reacted with mercuric oxide to form the mercurous salt which is decomposed by sodium carbonate. The mercuric salt, m. p. 164°, is obtained by adding a solution of mercuric acetate to a solution of benzoylformic acid. F. B.

Fixation of Unsaturated Molecules by Metals produced from their Organometallic Derivatives. A. JOB and R. REICH (*Compt. rend.*, 1923, **177**, 1439—1441).—On keeping a solution of

ferrous ethyl iodide (cf. A., 1922, i, 645), metallic iron is deposited as a mirror, ethylene and ethane also being formed. These changes are explained by the following scheme: $2FeEtI \longrightarrow FeEt_2+FeI_2 \longrightarrow 2C_2H_4+FeH_2+FeI_2 \longrightarrow C_2H_4+C_2H_6+Fe+FeI_2$, where ferrous hydride reduces ethylene to ethane. This explains why Wanklyn obtained ethylene and ethane from zinc ethyl and ferrous iodide. The iron deposit, which contains traces of ferrous ethyl iodide, is pyrophoric and decomposes water to give hydrogen.

Nickel, cobalt, chromium, and manganese are also produced in active forms from a halide salt and magnesium ethyl bromide, part of the metal being precipitated, the rest remaining in (colloidal) solution. Thus, when an ether–benzene solution of magnesium phenyl bromide is treated, in absence of air, with nickelous chloride, a solution is obtained which (1) rapidly absorbs carbon monoxide, in amount corresponding with the formation of nickel carbonyl, $Ni(CO)_4$; (2) slowly absorbs, per atom of nickel, 2 mols. of nitric oxide (giving a bluish-green solution); (3) absorbs ethylene (2 mols. for each atom of nickel) to give a reddish-brown solution; (4) absorbs acetylene ($Ni:3C_2H_2$); and (5) rapidly absorbs hydrogen ($2H_2:Ni$), nickel hydride being precipitated as a black, very reactive powder (cf. Schlenk and Weichselfelder, *Ber.*, 1923, **56**, [*B*], 2230).

E. E. T.

Organometallic Compounds. III. Compounds formed between Tin Alkyl Halides and Ammonia and the Amines. C. A. Kraus and W. N. Greer (*J. Amer. Chem. Soc.*, 1923, **45**, 3078—3083).—Tin trimethyl chloride forms a compound with 1 mol. of aniline, and with 1 mol. of pyridine (m. p. 37°). Tin trimethyl iodide combines with two equivalents of ammonia, one of which is loosely held, two equivalents of aniline, and one equivalent of pyridine. The compound with pyridine solidifies homogeneously at −17°. Tin dimethyl dichloride combines with two equivalents of pyridine. Mercury ethyl chloride and mercury amyl chloride each combine with one equivalent of ammonia. Solutions of the metal alkyl halides in amines are fair conductors of electricity, whilst the solutions in neutral solvents are virtually non-conductors. It is suggested that these compounds are of the ammonium type, $C_6H_5\cdot N<^{Sn(CH_3)_3}_{I}$.

F. B.

Organometallic Compounds. IV. Conductivity of Tin Trimethyl Chloride in Mixed Solvents. C. A. Kraus and W. N. Greer (*J. Amer. Chem. Soc.*, 1923, **45**, 2946—2954; cf. this vol., i, 25).—The electrical conductivity of tin trimethyl chloride in nitrobenzene and acetone solutions on the addition of small amounts of pyridine has been measured. A marked increase in conductivity takes place on the addition of pyridine, and this effect is greater the smaller the amount of pyridine already present. The conductivity of solutions of tin trimethyl chloride in mixtures of 0—100% of acetone and alcohol, nitrobenzene, and pyridine, respectively, has been measured at 25°. The initial conductivity in nitrobenzene is extremely low, indicating that tin trimethyl

chloride is not much ionised in this solvent. The initial conductivity in acetone is markedly higher than in nitrobenzene. Whilst the conductivity in acetone is increased on the addition of alcohol, this increase is much less marked than it is on the addition of pyridine. The results are in keeping with the view that tin trimethyl chloride itself is not a true electrolyte and that its electrolytic properties in solution are due to the formation of compounds of the oxonium and ammonium type, the tin trimethyl group transferring from chlorine to quadrivalent oxygen or quinquevalent nitrogen respectively. J. F. S.

The Conditions of Equilibrium and Motion of Molecules in Space. J. Böeseken (*Ber.*, 1923, **56**, [*B*], [2411—2414).—A discussion of the structures of *cyclo*hexane and *cyclo*heptane ring systems, in which a theory previously put forward (Derx, A., 1922, i, 651) is restated. The proof by Schrauth and Görig (A., 1923, i, 1084) that di*cyclo*hexane can exist in three forms is important in this connexion. E. H. R.

Ternary System Toluene–Acetone–Water. J. H. Walton and J. D. Jenkins (*J. Amer. Chem. Soc.*, 1923, **45**, 2555—2559).—The equilibrium curves for the system toluene–acetone–water have been determined experimentally at 0°, 20°, and 30°. It is shown that temperature has very little effect on the mutual solubility of the three components. J. F. S.

Catalytic Condensation of Acetylene with Benzene and its Homologues. J. S. Reichert and J. A. Nieuwland (*J. Amer. Chem. Soc.*, 1923, **45**, 3090—3091; cf. A., 1923, i, 753).—Diphenylethane, ditolylethane, and dixylylethane were prepared by passing acetylene into benzene, toluene, and xylene, respectively, at 10—20° in the presence of concentrated sulphuric acid and a mercuric salt. Similarly, dimesitylethane was prepared from mesitylene, and ethylidinebisethylbenzene from ethylbenzene. F. B.

The Disulphonation of Naphthalene. H. E. Fierz-David and A. W. Hasler (*Helv. Chim. Acta*, 1923, **6**, 1133—1146).—An extended account of work already published in brief (Fierz-David, A., 1921, i, 409; 1923, i, 1190). 1 : 5-Naphthalenedisulphonic acid crystallises in well-formed, monoclinic tablets, containing $4H_2O$, losing $2H_2O$ in a vacuum at 55°, and the remainder at 125°; m. p. 240—245° (decomp.). It is soluble in 0·98 part of water at 20°, and is not deliquescent. Its salts, with their solubilities in parts of water per part of anhydrous salt, are as follows: Li_2+2H_2O, monoclinic; Na_2+2H_2O, monoclinic, 9; K_2+2H_2O, monoclinic, 15; Rb_2, Cs_2, Tl_2 and $(NH_4)_2$ all anhydrous, monoclinic; $Ca+2H_2O$, triclinic, 40; $Sr+H_2O$, monoclinic (?), 96; $Ba+H_2O$, rhombic, 470; 250 at 100°; $Pb+3H_2O$, monoclinic, 82; Mg, (22), Zn (28), Co (46), Ni (73), Cu (21), all with $6H_2O$, form an isomorphous, monoclinic series. The *sulphonamide* forms small needles, m. p. above 310°, and the *sulphanilide* has m. p. 248—249°.

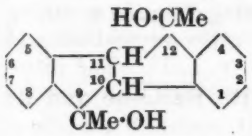
Naphthalene-1 : 6-disulphonic acid crystallises in large, monoclinic, striated prisms with $4H_2O$; it loses water gradually when

heated and melts at 125° (decomp.). It is deliquescent in damp air. The *sulphonamide* has m. p. 297—298°. The salts and their solubilities are as follows: Na_2+7H_2O, 3; K_2, 5; $(NH_4)_2+2H_2O$, 2; $Ca+4H_2O$, 10; $Sr+5H_2O$, 10; $Ba+3\frac{1}{2}H_2O$, 16; $Pb+4H_2O$, 12; all the foregoing are rhombic; Mg, Zn (3), Co (5), Ni (5), all with $6H_2O$, isomorphous, rhombic, $Cu+4H_2O$, 2.

Naphthalene-β-sulphonamide can be separated almost quantitatively from the α-compound or from disulphonamide by dissolving the mixed amides in 20% sodium hydroxide solution and cooling in ice, when the sodium salt of the β-sulphonamide crystallises out. The calcium salt of the 2 : 6-disulphonic acid can be precipitated quantitatively in the anhydrous form by heating its aqueous solution, alone or mixed with other calcium salts, in a closed vessel at 130°. E. H. R.

The Diphensuccindene Series. V. Colourless and Coloured 9 : 12-Dialkyl-$\Delta^{9,11}$-diphensuccindadienes. K. Brand and F. Schläger (*Ber.*, 1923, **56**, [*B*], 2541—2545; cf. A., 1912, i, 960; 1920, i, 486, 487).—An extension of previous work to compounds containing alkyl instead of aryl groups in the 9 : 12-positions.

Diphensuccindan-9 : 12-dione is converted by magnesium methyl iodide into 9 : 12-*dimethyldiphensuccindan*-9 : 12-*diol* (annexed formula), colourless needles, m. p. 170°. It is converted by boiling formic and glacial acetic acids into 9 : 12-*dimethyl*-$\Delta^{9,11}$-*diphensuccindadiene*, $\begin{matrix}CMe{=}C\cdot C_6H_4\\ |\\ C_6H_4\cdot C{=}CMe\end{matrix}$, dark red or yellowish-brown needles, m. p. 212°, which is hydrogenated in alcoholic solution in the presence of palladised charcoal to 9 : 12-*dimethyldiphensuccindane*, colourless needles, m. p. 94°. 9 : 12-*Diethyldiphensuccindan*-9 : 12-*diol* forms coarse, colourless crystals, m. p. 102°. It is transformed by a boiling mixture of formic and glacial acetic acids into 9 : 12-*diethylidenediphensuccindane*, slender, colourless needles, m. p. 199·5° (which is oxidised by chromic acid to acetaldehyde and diphensuccindandione) and 9 : 12-*diethyl*-$\Delta^{9,11}$-*diphensuccindadiene*, red or reddish-brown leaflets, m. p. 154° (indefinite). 9 : 12-*Dibenzyldiphensuccindan*-9 : 12-*diol*, small, colourless needles, m. p. 206°, is converted by acetic and formic acids into a mixture of coloured 9 : 12-dibenzyl-$\Delta^{9,11}$-diphensuccindadiene (which could not be isolated in the homogeneous condition) and 9 : 12-*dibenzylidenediphensuccindane*, colourless needles, m. p. 255°; the latter substance is oxidised by chromic acid to benzoic acid and diphensuccindan-9 : 12-dione, m. p. 202°. H. W.



The Diphensuccindene Series. VI. 9 : 12-Dinaphthyl Derivatives of the Diphensuccindene Series. K. Brand and K. Trebing (*Ber.*, 1923, **56**, [*B*], 2545—2547; cf. preceding abstract).—Diphensuccindadione is transformed by magnesium α-naphthyl bromide in the presence of ether and benzene into 9 : 12-*di*-α-*naphthyldiphensuccindan*-9 : 12-*diol*, colourless needles, m. p. 244°, which is converted by a boiling mixture of acetic and formic acids

into naphthalene and diphensuccindan-9 : 12-dione. 9 : 12-*Di*-β-*naphthyldiphensuccindan*-9 : 12-*diol*, colourless needles, m. p. 286—287°, is transformed under similar conditions into 9 : 12-*di*-β-*naphthyl*-$\Delta^{9,11}$-*diphensuccindadiene*, reddish-brown leaflets, m. p. 266°. The hydrocarbon is oxidised by chromic acid to *o*-β-naphthoylbenzoic acid, m. p. 168° (cf. Pickles and Weizmann, P., 1905, 20, 201), which is converted by concentrated sulphuric acid into 1 : 2-naphthanthraquinone, m. p. 168°; it is hydrogenated in the presence of alcohol and palladised charcoal to 9 : 12-*di*-β-*naphthyldiphensuccindane*, slender, colourless needles, m. p. 225°.

Magnesium 2-methoxy-α-naphthyl iodide appears to react normally with diphensuccindandione, but the action of water on the product gives naphthyl methyl ether and diphensuccindandione.

H. W.

Some Colouring Matters Derived from Bidiphenylenethylene. F. KEHRMANN and C. BUFFAT (*Helv. Chim. Acta*, 1923, **6**, 955—956).—The red hydrocarbon bidiphenylenethylene (A., 1896, i, 565) is readily sulphonated by concentrated sulphuric acid, forming a soluble sulphonic acid having an intense orange colour which dyes wool and silk in the same way as other acid dyes. The hydrocarbon can be nitrated in glacial acetic acid; two *dinitro*-derivatives were obtained, one forming deep red granules, sparingly soluble in alcohol, m. p. 171°, the other crystallising in orange-red prisms, more soluble in alcohol, m. p. 170°. The nitro-compounds can be reduced to amino-derivatives which form orange-coloured hydrochlorides.

E. H. R.

2-Nitro- and 2-Amino-cymene. W. A. DEMONBREUN and R. E. KREMERS (*J. Amer. Pharm. Assoc.*, 1923, **12**, 296—300).—For the nitration of cymene, 67 g. is added to an equal weight of sulphuric acid, cooled with ice, and the mixture is stirred until 0° is reached. A cooled mixture of 105 g. of sulphuric acid and 50 g. of nitric acid is then added, drop by drop, with constant stirring, common salt being occasionally mixed with the ice. About six hours are required for the reaction. After being stirred for a further thirty minutes, the mixture is poured into an equal volume of cold water. The oily layer is washed with water and fractionally distilled, the heavier fraction having b. p. 130—135°/14 mm., d^{22} 1·0355, n_D^{22} 1·5290. Reduction by tin or iron and hydrochloric acid gave 2-aminocymene, d^{22} 0·9448, n_D^{22} 1·5395 (hydrochloride, m. p. 206—207°; acetyl derivative, m. p. 70—71°).

CHEMICAL ABSTRACTS.

β-Naphthylamine-5 : 7- and -6 : 8-disulphonic Acids. H. E. FIERZ-DAVID and M. BRAUNSCHWEIG (*Helv. Chim. Acta*, 1923, **6**, 1146—1151).—A number of salts of these two acids were prepared in the hope of discovering some method of separating the two acids superior to that previously described (Fierz, "Farbenchemie," 2nd ed., p. 43). Although a separation can be effected through the magnesium salts, it offers no advantages.

β-Naphthylamine-5 : 7-disulphonic acid crystallises with $5H_2O$

in well-formed rhombic needles (from hydrochloric acid) or glistening leaflets (from water). It loses its water completely at 150°. The following salts are described, with solubilities at 20° in g. per 100 g. of saturated solution: Na_2+6H_2O, felted needles which melt in the hand, 72·2; $NaH+4H_2O$, rhombic needles, 7·91; K_2+2H_2O, rosettes of rhombic needles, 63·9; $KH+4H_2O$, short, rhombic prisms, 2·58; $(NH_4)_2+3H_2O$, rhombic prisms, 68·1; $Ca+4H_2O$, monoclinic prisms, 40·2; $Sr+4H_2O$, 29·48, $Ba+3H_2O$, 22·7; the following all crystallise in well-formed rhombic needles or prisms: $Mg+8H_2O$, 21·09; $Zn+8H_2O$, 39·4; $Co+8H_2O$, 29·4; $Pb+6H_2O$, 48·1; $Ni+6H_2O$, 35·5. The solubility of the free acid is 22·97.

β-Naphthylamine-6 : 8-disulphonic acid crystallises with $4H_2O$ in small, monoclinic needles, solubility 9·24 g. per 100 g. of saturated solution at 20°. The following salts are described: Na_2+3H_2O, well-formed prisms, 59·04; $NaH+4H_2O$, long, thin needles, 7·46; K_2+2H_2O, lustrous prisms, 51·6; $KH+2H_2O$, long, rhombic prisms, 2·47; $(NH_4)_2+2H_2O$, monoclinic, 70·35; the alkaline-earth metal salts are isomorphous, monoclinic, with $3H_2O$,Ca, 29·1, Sr, 20·8, Ba, 12·0; $Mg+8H_2O$, 8·7, $Zn+8H_2O$, 34·5; $Co+8H_2O$, 27·96; $Ni+6H_2O$, monoclinic prisms, 33·2; $Pb+H_2O$, 44·5, aggregates of small needles.

The preparation of the two acids from β-naphthylamine is described in detail. E. H. R.

Chloroamidines. Paul Robin (*Compt. rend.*, 1923, **177**, 1304—1306).—Alkali hypochlorites convert amidine hydrochlorides, in aqueous solution, into chloroamidines (cf. Bougault and Robin, A., 1920, i, 568). Thus, benzamidine affords *benzochloroamidine*, $NH_2{\cdot}CPh{:}NCl$ or $NHCl{\cdot}CPh{:}NH$, colourless, odourless needles, not affected by heating up to 100°. It may be crystallised from alcohol, but when heated with this solvent at 100°, in a closed tube, affords benzamidine and a volatile chloro-compound. With boiling dilute acids, benzochloroamidine gives chlorine, whilst with aqueous potassium iodide solution, one mol. of the amidine gives 2 atoms of iodine. When heated with water at 100° in a closed tube, the chloroamidine affords a mixture of cyaphenin, $(Ph{\cdot}CN)_3$, benzonitrile, benzoic acid, ammonia, and benzamidine. Benzochloroamidine does not react with antipyrine, but is converted by acetic anhydride, in boiling benzene solution, into an *acetyl* derivative, m. p. 122°, in which the chlorine is still reactive towards potassium iodide.

p-*Tolylchloroamidine* and *benzylchloroamidine*, $CH_2Ph{\cdot}CN_2H_2Cl$, melt, respectively, at 96° and 72°. E. E. T.

Preparation of Amidines. Chemische Fabriken vorm. Weiler ter Meer (D.R.-P. 372842; from *Chem. Zentr.*, 1923, [iv], 661).—Acetanilide, its derivatives, homologues, or analogous compounds, with the exception of arylglycine anilides, are treated with carbonyl chloride in the presence or absence of condensing reagents. The following reaction is typical: $2NHPh{\cdot}COMe+COCl_2=HCl+CO_2+COMe{\cdot}Cl+NHPh{\cdot}CMe{:}NPh$. The reaction proceeds smoothly

without the formation of by-products. Acetanilide and carbonyl chloride give, as above, diphenylacetamidine hydrochloride. *p*-Acetotoluidide and carbonyl chloride yield pp′-*ditolylacetamidine*, m. p. 122°. oo′-*Ditolylacetamidine* forms flat needles, m. p. 65°. Acetyl compounds of the amines of alkoxylated or halogenated hydrocarbons, or of polynuclear or condensed hydrocarbons may also be used. *α-Dinaphthylacetamidine* is crystalline and has m. p. 137°. G. W. R.

Basic Derivatives of *p*-Aminophenyl Ethyl Ether. Society for Chemical Industry in Basle (Swiss Pats. 96389, 96606, and 96607; from *Chem. Zentr.*, 1923, iv, 662—663).—*p*-Acetaminophenol halogenethyl ethers $NHAc{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CH_2X$ or their derivatives alkylated in the nucleus, obtained by acting on alkali acetamidophenoxides with ethylene dihalogenides, are allowed to react with secondary aliphatic amines. p-*Acetamidophenyl β-bromoethyl ether*, crystals, m. p. 130°, gives with diethylamine p-*acetamidophenyl* β-*diethylaminoethyl ether*; the *hydrochloride* forms small needles, m. p. above 200°. *p*-Acetamidophenyl β-bromoethyl ether gives with piperidine p-*acetamidophenyl* 2-*piperidylethyl ether*; *the hydrochloride* forms crystals, m. p. 252°. From 4-*acetamido*-2-*allylphenyl* β-*chloroethyl ether*, crystals, m. p. 60°, and diethylamine, 4-*acetamido*-2-*allylphenyl* β-*diethylaminoethyl ether*, m. p. 70°, is obtained; its *hydrochloride* is crystalline and has m. p. 149°. G. W. R.

Methyl Sulphites of Secondary Aromatic Aliphatic Amines. Farbwerke vorm. Meister, Lucius, & Brüning (Austr. Pat. 93319; from *Chem. Zentr.*, 1923, iv, 802; cf. Bockmühl and Windisch, A., 1923, i, 29).—The compounds obtained by earlier patents may also be prepared by *N*-alkylation of the methyl sulphites obtained from primary aromatic amines and a hydrogen sulphite compound of formaldehyde. Examples are given of the preparation of sodium 1-phenyl-2 : 3-dimethylpyrazole-5-one-4-ethylaminomethyl sulphite and sodium *N*-ethylphenetidine methyl sulphite. G. W. R.

[Alkali Metal as a Reagent for Weakened Valencies in Organic Compounds.] K. Ziegler and F. Thielmann (*Ber.*, 1923, **56**, [*B*], 2453).—In their communication on this subject (A., 1923, i, 921), the authors have overlooked the fact that a portion of the work has been described previously by Marcus (*Diss.*, Jena, 1914). H. W.

The Preparation of ββ′-Dinaphthyl Ether. V. M. Rodionov and S. J. Manzov (*J. Soc. Chem. Ind.*, 1923, **42**, 509—510T).—During the distillation of crude naphthol on the technical scale, the formation of a large proportion of ββ′-dinaphthyl ether was observed. The cause of this was traced to the presence of inorganic salts, particularly acid salts, during the distillation. When β-naphthol is heated at 200—210° for about ten hours, it is converted entirely into ββ′-dinaphthyl ether. E. H. R.

Substitution Products of Diphenylene Oxide. II. W. BORSCHE and B. SCHACKE (*Ber.*, 1923, 56, [*B*], 2498—2508; cf. Borsche and Bothe, A., 1908, i, 528).—An extension of previous work. In consequence of the communication of Mayer and Krieger (A., 1922, i, 746), the compound described previously (*loc. cit.*) as 3-nitrodiphenylene oxide is now considered to be the 2-nitro-derivative.

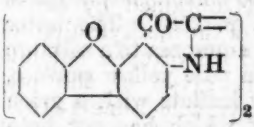
The nitration of diphenylene oxide in glacial acetic acid solution gives a mixture of 2-nitrodiphenylene oxide and 3(?)-*nitrodiphenylene oxide*, small, yellow needles, m. p. about 110°. The former compound is reduced by sodium and methyl alcohol to 2 : 2′-*azoxydiphenylene oxide*, pale yellow, matted needles, m. p. 259—260°, and by sodium and boiling amyl alcohol to 2 : 2′-*azodiphenylene oxide*, m. p. 282°. It is converted by concentrated sulphuric acid into 2-nitrodiphenyleneoxidesulphonic acid, $NO_2 \cdot C_{12}H_6O \cdot SO_3H$, which is isolated in the form of its *sodium* salt, pale yellow needles. The salt is converted by phosphorus pentachloride into 2-*nitrodiphenyleneoxidesulphonyl chloride*, m. p. about 200° (decomp.), which is transformed by ammonia into the corresponding *amide*, an amorphous, white powder, m. p. (indefinite) 265° (decomp.). The action of tin and concentrated hydrochloric acid on sodium 2-nitrodiphenyleneoxidesulphonate yields 2-*aminodiphenyleneoxidesulphonic acid*, the *barium* salt of which, colourless leaflets, is described.

2-Aminodiphenylene oxide is converted by ethyl bromomalonate into *ethyl diphenyleneoxide-2-aminomalonate*,

$$C_{12}H_7O \cdot NH \cdot CH(CO_2Et)_2,$$

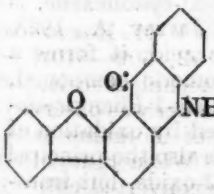
pale yellow needles, m. p. 100°; it is transformed when heated at 240° into *ethyl diphenyleneoxideindoxylate*,

$$C_{12}H_6O\langle \begin{matrix} CO \\ NH \end{matrix} \rangle CH \cdot CO_2Et,$$



m. p. 191°, which when fused with alkali hydroxide yields "*bisdiphenyleneoxide-indigo*," a bluish-black powder which remains unchanged below 350°; the annexed formula is assigned to it, but the possibility of the formation of the new ring in the 2 : 3-position is not excluded.

2-*Diphenyleneoxide-2′-aminobenzoic acid*, $C_{12}H_7O \cdot NH \cdot C_6H_4 \cdot CO_2H$, pale yellow needles, m. p. 227°, is obtained by heating *o*-chlorobenzoic acid, 2-aminodiphenylene oxide hydrochloride, potassium carbonate, and copper bronze in the presence of amyl alcohol at 140—150°. It passes when heated with zinc chloride at 240° into 2-*anilinodiphenylene oxide*, $C_{12}H_7O \cdot NHPh$, colourless leaflets, m. p. 132°; the acid is transformed by the successive action of phosphorus pentachloride and aluminium chloride into *phenylene oxideacridone*, $C_{19}H_{11}O_2N$, greenish-yellow leaflets, m. p. above 350° (annexed formula).



2-Diacetamidodiphenylene oxide is converted by nitric acid in glacial acetic acid solution into 3(?)-*nitro-2-diacetamidodiphenylene oxide*, yellow leaflets, m. p. 196—197°, which is hydrolysed by alcohol and fuming hydrochloric acid into 3(?)-

nitro-2-aminodiphenylene oxide, orange-red needles, m. p. 222°. 2 : 3(?)-*Diaminodiphenylene oxide* forms colourless crystals, m. p. 166° (*hydrochloride*, colourless leaflets); it is characterised as an orthodiamine by its ability to condense with benzil to give the quinoxaline *derivative*, $C_{12}H_6O<\begin{matrix}N{:}CPh\\N{:}CPh\end{matrix}$, greenish-yellow needles, m. p. 179°, and with phenanthraqinone to give the *compound*, $C_{12}H_6O<\begin{matrix}N{:}C\cdot C_6H_4\\N{:}C\cdot C_6H_4\end{matrix}$, yellow needles, m. p. 297°.

The action of aluminium chloride on diphenylene oxide and acetyl chloride in the presence of carbon disulphide leads to the formation of 3-acetyldiphenylene oxide and 3 : 6(?)-*diacetyldiphenylene oxide*, colourless needles, m. p. 140°. *Nitro-3-acetyldiphenylene oxide*, a brown, crystalline powder, m. p. 105°, 3-*ethyldiphenylene oxide*, a colourless liquid, b. p. 310°/atmospheric pressure, and *nitro-3-ethyldiphenylene oxide*, yellow needles, m. p. 96°, b. p. 218—226°/15 mm., are described. Diacetyldiphenylene oxide yields a *dioxime*, $C_{16}H_{14}O_3N_2$, a colourless, sandy powder, m. p. 250° (decomp.), which is isomerised by phosphorus pentachloride in the presence of ether into *diacetylaminodiphenylene oxide*, colourless leaflets, m. p. 258°, from which *diaminodiphenylene oxide*, slender, colourless needles, m. p. 213°, is obtained. *Diethyldiphenylene oxide*, a colourless, odourless liquid, b. p. 197—199°/20 mm., 334°/750 mm., is prepared by the action of amalgamated zinc and hydrochloric acid on diacetyldiphenylene oxide.

Diphenylene oxide is converted by phthalic anhydride in the presence of nitrobenzene and aluminium chloride into diphenyleneoxidephthalonic acid, m. p. 203—204°, which passes under the influence of anhydrous zinc chloride at 260° into *phthaloyldiphenylene oxide*, $C_{20}H_{10}O_3$, greenish-yellow needles, m. p. 258°. The latter substance is reduced by zinc dust and aqueous ammonia to a mixture of *phenyleneoxidedihydroanthranol*, $C_{20}H_{14}O_2$, a pale yellow powder, m. p. 169°, and a *compound*, $C_{20}H_{12}O$, yellow leaflets with a green fluorescence, m. p. 311°, the constitution of which has not been elucidated. *Diphthaloyldiphenylene oxide*, $C_{28}H_{12}O_5$, crystallises in slender, greenish-yellow needles, m. p. 295°. H. W.

The Configuration of Cyclic 1 : 2-Diols. J. Böeseken (*Ber.*, 1923, **56**, [*B*], 2409—2411).—Methods previously described (cf. Derx, A., 1922, i, 651) have been applied to the determination of the configuration of isomerides of 1-methyl-, 1-phenyl-, and 1-*cyclo*hexyl-*cyclo*hexane-1 : 2-diols. The 1-methyl*cyclo*hexane-1 : 2-diol, m. p. 67°, obtained by oxidation of 1-methyl-Δ^1-*cyclo*hexene, is the *cis*-compound (not *trans*, see Nametkin and Jarzev, A., 1923, i, 1081). With potassium hydroxide and boric acid, it forms a crystalline *salt*, $C_6H_9Me{:}O_2{:}BOK,4H_2O$. The isomeric compound, m. p. 84°, has therefore the *trans*-configuration. *cis*-1-Phenyl*cyclo*hexane-1 : 2-diol is the product, m. p. 95°, obtained by oxidation of 1-phenyl-Δ^1-*cyclo*hexene with permanganate. It is also the principal product of hydrolysis of 1-phenyl*cyclo*hexene 1 : 2-oxide, but trans-1-*phenyl*cyclo*hexane*-1 : 2-*diol* is also formed in the reaction product;

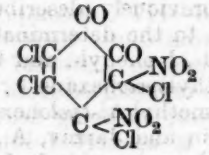
it forms short prisms, m. p. 98·5°. It is probably the primary product, but under the experimental conditions isomerises into the *cis*-form (cf. Nametkin and Ivanov, A., 1923, i, 1097). cis-1-cyclo*Hexyl*cyclo*hexane*-1 : 2-*diol*, m. p. 122—123°, is obtained by oxidation of the corresponding *cyclo*hexene, and the trans-*isomeride*, m. p. 142°, by hydration of 1-*cyclo*hexyl*cyclo*hexene 1 : 2-oxide.

E. H. R.

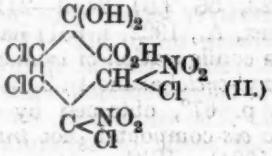
Action of Nitric Acid and Nitrogen Peroxide on Tetrachloro- and Tetrabromo-pyrocatechol and the Corresponding Quinones. T. ZINCKE (*Annalen*, 1923, **435**, 145—173).—Tetrachloro-*o*-benzoquinone, when treated with nitric acid (*d* 1·4—1·51) gives, according to the concentration of the acid, one of two *compounds*: *A*, $C_6H_4O_5Cl_4$ or *B*, $C_6H_4O_8N_2Cl_4$, which are also produced under similar conditions from tetrachloropyrocatechol. The former (*A*), colourless needles, m. p. 95—96°, is a trihydrate of a tri-keto-compound; when heated, it is converted into trichlorohydroxy-*p*-benzoquinone, and, on reduction, gives trichlorohydroxyquinol (cf. [Frl.] Weishaupt, *Dissert.*, Marburg, 1923).

Compound *B* forms white needles, decomposing at the m. p. (114—115°) to give water, carbon dioxide, oxides of nitrogen, and the compound, $C_{10}O_2Cl_8$, described previously (A., 1909, i, 591; 1912, i, 964). The last compound is formed intermediately on boiling an aqueous solution of *B*, then decomposing to give perchloroindone. Similarly, on heating a solution of *B* in alcohol, acetone, or acetic or concentrated sulphuric acids, the compound $C_{10}O_2Cl_8$ is formed.

Compound *B*, when treated with alkali, affords a number of decomposition products, depending on the concentration of alkali, etc. Products identified include ammonia, nitrogen, carbon dioxide, and oxalic and nitrous acids. Mainly from this decomposition, and from the fact that compound *B* is also produced (here not accompanied by *A*) by treating tetrachloropyrocatechol at 0° with liquid nitrogen peroxide, the constitution II is assigned to *B*, the formation of this substance from tetrachloropyrocatechol proceeding through the corresponding quinone and its nitrogen peroxide additive compound I:



(I.)



(II.)

(One NO_2-group is probably nitro-, the other nitrite, ·ONO).

A low value is obtained for the molecular weight of *B* when determined cryoscopically in acetic acid owing to the dissociation of the hydrate (II).

Whilst tetrachloro-*o*-benzoquinone does not afford compound (I) (but only tarry products) when treated with nitrogen peroxide,

the constitution (II) assigned to *B* falls into line with the above decomposition in presence of alkali. In this process, chloro-groups and a nitrite group are replaced by hydroxyl, oxalic acid and the compound, $OH\cdot CH{:}C(OH)\cdot C(OH)_2\cdot CH(OH)_2$ resulting. Further decomposition affords *s*-dihydroxyethylene, or the isomeric glycollaldehyde, and glyoxylic acid, whence carbon dioxide and more oxalic acid are produced.

When substance *B* is treated with aniline or phenylhydrazine, red or dark-coloured *substances* result, respectively.

Tetrabromo-*o*-benzoquinone behaves unlike the chloroquinone towards nitric acid, white, insoluble *products* being formed. Tetrabromopyrocatechol is, however, converted by nitric acid into a *compound*, $C_6H_4O_5Br_4$ (type *A*) which decomposes partly to give a *substance*, $C_5O_2Br_4$, m. p. 142—143°. Bromo-compounds corresponding with *B* result when tetrabromopyrocatechol is treated with nitrogen peroxide, no compound of type *A* being produced in this case.

The *bromo*-compound, $C_6H_2O_7N_2Br_4,H_2O$ (type *B*), which forms colourless needles, m. p. 113—114° (decomp.), on drying undergoes partial decomposition (the m. p. rising to 126—127°). On keeping, or on warming in solution in glacial acetic, sulphuric, or formic acids, the bromo-compound affords the substance $C_{10}O_2Br_8$; on boiling in aqueous solution, it gives perbromoindone; whilst with alkalis the bromo-compound decomposes in a manner similar to that observed with the corresponding chloro-compound (*B*).

When halogenated pyrocatechols are treated with mixed acid (HNO_3, 88·9%, H_2SO_4, 9·9%, H_2O, 1·2%), type *A* is produced to a greater extent than when nitric acid alone is used, owing to increased oxidation. The corresponding quinones, when treated with mixed acid, give in the case of the chloro-compound, tarry products, and in that of the bromo-compound, decomposition products of the intermediately-formed *substance*, $C_6H_4O_5Br_4$.

3 : 4 : 6-Trichloro-5-methyl- and 3 : 4 : 5-trichloro-6-methyl-pyrocatechol are converted into compounds of type *B* (but not of type *A*), $C_6H_4O_8N_2Cl_3Me$, when treated with nitric acid (*d* 1·45—1·48), or with nitrogen peroxide, indifferent results being obtained using mixed acid.

The *compound*, $C_6H_4MeO_8N_2Cl_3$, obtained from the 3 : 4 : 6-derivative, forms white needles, m. p. 116—117° (decomp.) (one specimen, m. p. 110—111°), crystallised from dilute hydrochloric acid. After careful drying, the m. p. rises to 126—127°, this m. p. being obtained when the substance is crystallised from nitric acid. The compound, on melting, or, better, on being heated in glacial acetic or sulphuric acid solution, is converted into the substance, $C_{10}O_2Cl_6Me_2$ (m. p. 182°), described previously (A., 1897, i, 507). From the decomposition, in presence of alkali, of the compound $C_6H_4MeO_8N_2Cl_3$, the latter is given the constitution $NO_2\cdot CHCl\cdot CCl(NO_2)\cdot CMe{:}CCl\cdot C(OH)_2\cdot CO_2H$.

The isomeric *compound*,

$$NO_2\cdot CHCl\cdot CCl(NO_2)\cdot CCl{:}CMe\cdot C(OH)_2\cdot CO_2H,$$

obtained from 3 : 4 : 5-trichloro-6-methylpyrocatechol, forms

needles, melting at 115—116° (or, after drying, 125—126°) to give the substance $C_{10}O_2Cl_6Me_2$, which is more readily obtained by heating the first compound in aqueous, acetic, or sulphuric acid solution, and is identical with a compound (m. p. 175°) previously described (A., 1897, i, 509).

The substance, $C_{10}O_2Cl_8$, mentioned above, which is also obtained from the nitric acid decomposition product ($C_6HO_6N_2Cl_4Me$) of tetrachloro-*o*-cresol by warming with concentrated sulphuric acid, has been re-investigated. It was previously stated that it was converted by boiling methyl alcohol into the compound $C_9Cl_6(OH)\cdot OMe$ (m. p. 138°), which is now written as $C_{10}O_2Cl_7\cdot OMe$ (m. p. 136—137°).

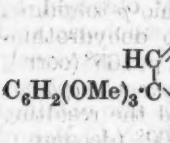
The constitution of the compound $C_{10}O_2Br_8$ (cf. A., 1907, i, 322; 1912, i, 964) is still unsettled, but the possibility of it being a derivative of tetrahydronaphthalene is excluded. The compound, on melting at 207—208°, on heating with glacial acetic acid and sodium acetate, or on heating in nitrobenzene solution, affords perbromoindone (m. p. 195—196°), the latter being converted by warm aniline into the *anilide*, $C_9OBr_5\cdot NHPh$, scarlet leaflets, m. p. 224° (decomp.). E. E. T.

The Constitution of Weselsky and Benedict's Dinitroquinol Methyl Ether. F. KEHRMANN and G. JEQUIER (*Helv. Chim. Acta*, 1923, **6**, 949—951).—The constitution of this ether given by Reverdin and de Luc (A., 1911, i, 965), who concluded that it is 3 : 5-dinitro-4-hydroxyanisole, has been confirmed by the preparation of the isomeric ether. The silver salt of 3 : 5-dinitroquinol 1-acetate reacts with methyl iodide to give 2 : 6-*dinitro*-4-*acetoxyanisole*, small, yellow crystals, m. p. 63°, which when hydrolysed gives 2 : 6-*dinitro*-4-*hydroxyanisole*, yellow crystals, m. p. 149°. The dinitroquinol monoacetate used for the preparation was obtained by nitration of quinol diacetate (see following abstract). E. H. R.

The Action of Nitric Acid on Quinol Diacetate. F. KEHRMANN and W. KLOPFENSTEIN (*Helv. Chim. Acta*, 1923, **6**, 952—954).—Nitration of quinol diacetate with fuming nitric acid below 10° gives, not 3 : 5-dinitroquinol diacetate, as stated by Nietzki and Preusser (A., 1887, 574), but 3 : 5-*dinitroquinol* 1-*monoacetate*, yellow tablets, m. p. 94°. Acetylation of this with acetic anhydride gives 3 : 5-*dinitroquinol diacetate*, colourless needles, m. p. 134°. More careful nitration of quinol diacetate at 0° gives 3-*nitroquinol* 1-*acetate*, lemon-yellow needles, m. p. 84°. This can be acetylated to 3-*nitroquinol diacetate*, colourless needles, m. p. 80°. It is evident that nitration of quinol diacetate cannot proceed without elimination of one acetyl group. E. H. R.

Some Condensation Products of Hydroxyquinol Trimethyl Ether. T. SZÉKI (*Ber.*, 1923, **56**, [*B*], 2464—2468).—Hydroxyquinol trimethyl ether condenses with acetone in glacial acetic acid solution in the presence of concentrated sulphuric acid to give

2 : 4 : 5 : 2′ : 4′ : 5′-*hexamethoxydiphenylisophorone* [1 : 5 : 5-*trimethyl*-3 : 3-*bis*-2′ : 4′ : 5′-*trimethoxyphenyl*-Δ^1-cyclo*hexene*] (annexed formula) colourless needles, m. p. 207°, which is converted by bromine in glacial acetic acid solution into the bromo-*derivative*, $C_{27}H_{36}O_6Br_2$, colourless, lustrous crystals, m. p. 119°; as by-product of the condensation, 2 : 4 : 5-*trimethoxybenzenesulphonic acid*, colourless needles, m. p. 115°, is obtained, the *sodium* salt of which is described.



The action of hydrogen chloride on a solution of 2 : 4 : 5-trimethoxybenzene and alloxan in alcohol leads to the production of 2 : 4 : 5-*trimethoxyphenyldialuric acid*,

$$CO<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>C(OH)\cdot C_6H_2(OMe)_3,$$

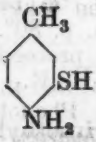
small, colourless needles, m. p. 248—249° (decomp.). It is converted by acetic anhydride and sulphuric acid monohydrate into the corresponding *acetate*, decomp. 270—292°, and is decomposed by boiling *N*/5 sodium hydroxide solution into ammonia, carbon dioxide, and 2 : 4 : 5-*trimethoxyphenyltartronimide*,

$$NH<\begin{matrix}CO\\CO\end{matrix}>C(OH)\cdot C_6H_2(OMe)_3,$$

colourless, microscopic leaflets, m. p. 220—221°. 2 : 4 : 5-*Trimethoxyphenacyldialuric acid*, slender, colourless crystals, m. p. 245° (decomp.) after darkening at 220°, is prepared from 2 : 4 : 5-trimethoxyacetophenone and alloxan.

Benzhydrol is converted by 2 : 4 : 5-trimethoxybenzene in alcoholic solution in the presence of hydrogen chloride into 2 : 4 : 5-*trimethoxytriphenylmethane*, $C_6H_2(OMe)_3\cdot CHPh_2$, colourless needles, m. p. 117°. In a similar manner, 2 : 4 : 5 : 4′-tetramethoxydiphenylcarbinol and 2 : 4 : 5-trimethoxybenzene yield 2 : 4 : 5 : 2′ : 4′ : 5′ : 4″-*heptamethoxytriphenylmethane*, slender, colourless needles, m. p. 162°, whereas 2 : 4 : 5-trimethoxyphenyl-α-naphthylcarbinol and 2 : 4 : 5-trimethoxybenzene give 2 : 4 : 5 : 2′ : 4′ : 5′-*hexamethoxydiphenyl-α-naphthylmethane*, slender, colourless needles, m. p. 198°. H. W.

Action of Sulphur on *p*-Toluidine in the Presence of Litharge. Thio-*p*-toluidine, its Constitution and some of its Derivatives. M. T. BOGERT and M. R. MANDELBAUM (*J. Amer. Chem. Soc.*, 1923, **45**, 3045—3055).—The formation of thio-*p*-toluidine by heating *p*-toluidine with sulphur at 140° in the presence of litharge takes place through the mercaptan (annexed formula) which reacts with a nuclear hydrogen atom of unchanged *p*-toluidine. A small proportion of the mercaptan was oxidised to dithio-*p*-toluidine, m. p. 88·5°, acetyl derivative, m. p. 213°. The sulphide produced by de-amination of thio-*p*-toluidine was identical with di-*m*-tolyl sulphide synthesised from *m*-iodotoluene and sodium *m*-tolyl sulphide. The respective sulphones and a mixture of them melted at 94°. In the absence of litharge and



at 180—220°, the intermediate mercaptan reacted with the methyl group of unchanged *p*-toluidine to give dehydrothio-*p*-toluidine. The authors failed to convert thio-*p*-toluidine into dehydrothio-*p*-toluidine. The former gave a *diacetyl* derivative, m. p. 165° (corr.), which was oxidised to *bis-2-acetamido-5-carboxyphenylsulphone*, m. p. above 360°. The latter was de-acetylated and the resulting *bis-2-amino-5-carboxyphenylsulphone* melted above 360° (decomp.); the *methyl* ester forms thin, square, colourless tablets, m. p. 234° (corr.), the *ethyl* ester forms yellow, transparent prisms, m. p. 206° (corr.). F. B.

Formation of Liquid Crystals of Mixtures of Cholesterol and Cetyl Alcohol. A. Mlodziejowski (*Z. Physik*, 1923, **20**, 317—342).—The conditions necessary for the production of liquid crystals of mixtures of cholesterol and cetyl alcohol and the approximate character of the equilibrium diagram relating to the phases of mixtures of these substances have been determined. Cholesterol exists in two solid enantiomorphic modifications, the transformation temperature associated with which is about 43°. Liquid cetyl alcohol on cooling deposits needle-shaped crystals at about 50°. Crystallisation is accompanied by the separation of an amorphous solid phase characterised by the presence of lenticular masses. The transformation from liquid to solid is reversible. Liquid crystals of mixtures of cholesterol and cetyl alcohol may be either homogeneous or may exhibit a spherolitic or myelin structure characterised by the presence of rod-like, biscuit- or worm-shaped masses in a state of agitation. Of these two varieties of liquid crystals, the homogeneous variety is the more stable. Cetyl alcohol is practically insoluble in this modification. The liquid crystals are probably composed of equal molecular proportions of the two components, and on heating are reversibly converted into solid crystals provided the concentrations of the components are within certain limits. They form an eutectic mixture with cetyl alcohol. J. S. G. T.

Preparation of Nucleus-substituted Hydroxyl Derivatives of β-Amino-α-hydroxy-α-arylethanes and β-Amino-α-bisarylethanes. O. Hinsberg (D.R.-P. 373286; from *Chem. Zentr.*, 1923, iv, 662; cf. A., 1923, i, 923).—Phenols, naphthols, or their substitution products are allowed to react with aminoacetal or its *N*-mono- or di-alkylated derivatives in the presence of hydrochloric acid under pressure. For example, with equimolecular proportions of phenol and aminoacetal, in the presence of hydrochloric acid under pressure at 100°, the following reaction takes place: $PhOH+NH_2\cdot CH_2\cdot CH(OEt)_2+HCl+H_2O=$
$OH\cdot C_6H_4\cdot CH(OH)\cdot CH_2\cdot NH_2,HCl+2EtOH.$
α-p-*Hydroxyphenyl-β-aminoethanol* thereby obtained has m. p. above 250°; the *hydrochloride* has m. p. 172° (decomp.). Phenol (2 mols.) and aminoacetal (1 mol.) give *β-amino-α-bis*(p-*hydroxyphenyl*)*ethane*, which has m. p. 105°. Pyrocatechol and methylaminoacetal yield *o*-dihydroxyphenylethanolmethylamine (adrenaline). *p*-Cresol and aminoacetal give *β-amino-α-hydroxy-α*-1-

hydroxy-4-methylphenylethane, an unstable compound which gives a *hydrochloride* with m. p. 120° (decomp.). G. W. R.

Naphthenic Acid. III. Naphthenic Acids from Kubiki Kerosene Distillate. Y. TANAKA and S. NAGAI (*J. Chem. Ind. Japan*, 1923, **26**, 1115—1123; cf. *ibid.*, 1923, **26**, 309; A., 1923, i, 464).—A crude mixture of acid substances was obtained by acidifying a waste lye obtained in the refining of kerosene distillate from crude oil produced at Kubiki. Crude naphthenic acids (d_4^{15} 0·9647, n_D^{15} 1·4790, and acid value 202·8) were then obtained by three methods. About 86% of the crude acids distilled at 140—210°/8·9—9 mm. The lower distillates contained some phenolic compounds, and the fractions above 200° showed lower specific gravities than the preceding ones. The acid was converted into methyl esters, d_4^{15} 0·9368, n_D^{15} 1·4663, about 83% of which distilled at 120—180°/8·9—9 mm., and the fractions above 170° gave decreasing specific gravities. A mixture of pure naphthenic acids (d_4^{15} 0·9587, n_D^{15} 1·4707, and acid value 244·5) was obtained by saponifying the mixed esters, about 90% of which distilled at 150—210°/8·9—9 mm. The higher fractions above 200° showed again lower specific gravities than the preceding ones. The mixed naphthenic acids and their distillates of Kubiki origin have much smaller specific gravities than those of Kurokawa origin, which indicates the presence of isomerides having low specific gravities in the former. K. K.

Normal Ammonium Salts of some Organic Acids and their Substitution Derivatives. VIII. L. MCMASTER and P. K. PRATTE (*J. Amer. Chem. Soc.*, 1923, **45**, 2999—3001).—A description of normal ammonium salts of organic acids prepared by the method previously described (A., 1918, i, 263). The solubilities of the normal ammonium salts of the following acids are expressed in g. of salt per hundred g. of water, methyl alcohol, and ethyl alcohol in the order named. Phenoxyacetic acid 13·03, 3·97, 0·44, *p*-nitrophenylacetic acid 7·41, 15·14, 1·82, *o*-iodobenzoic acid 67·11, 184·10, 63·37, *o*-methoxybenzoic acid 38·25, 17·85, 4·82, 2 : 4-dinitrobenzoic acid 62·70, 21·39, 3·85, 5-nitrosalicylic acid 4·43, 4·41, 1·96, naphthalene-1-sulphonic acid 45·91, 34·45, 9·22, naphthalene-2-sulphonic acid 11·71, 8·33, 2·53, 2 : 5-dichlorobenzenesulphonic acid, 11·30, 20·15, 2·59, 6-chloro-3-nitrobenzenesulphonic acid 4·72, 2·76, 0·96. F. B.

3 : 5-Dinitrobenzoates of Phenols. R. C. BROWN and R. E. KREMERS (*J. Amer. Pharm. Assoc.*, 1922, **11**, 607—608).—3 : 5-Dinitrobenzoic esters of phenol (m. p. 145—146°), *o*-cresol (133—134°), *m*-cresol (160—162°), *p*-cresol (180—182°), guaiacol (138—139°), carvacrol (76—77°), and thymol (102—103°) were prepared as a means of identification of the phenols.

CHEMICAL ABSTRACTS.

Proteinogenous Amino-alcohols and Cholines. III. P. KARRER, E. HORLACHER, F. LOCHER, and M. GIESLER (*Helv. Chim. Acta*, 1923, **6**, 905—919; cf. A., 1922, i, 813).—*N*-Dimethyl-leucinol

[β-dimethylamino*iso*hexylalcohol] (cf. A., 1921, i, 228) condenses with *p*-nitrobenzoyl chloride in chloroform solution to give *p*-nitrobenzoyl-*N*-dimethyl-leucinol. This can be reduced to *p*-aminobenzoyl-*N*-dimethyl-leucinol, which, in the form of its hydrochloride, is a very powerful local anæsthetic. The corresponding *N*-diethyl, *N*-dipropyl, and *N*-pentamethylene [piperidino] compounds are likewise powerful local anæsthetics. Of the four, the *N*-diethyl compound is the most powerful, being eight times as active as novocaine and at the same time less poisonous than cocaine. p-*Nitrobenzoyl*-N-*dimethyl-leucinol hydrochloride*,

$$CHMe_2 \cdot CH_2 \cdot CH(NMe_2,HCl) \cdot CH_2O \cdot CO \cdot C_6H_4 \cdot NO_2,$$

forms yellow needles, m. p. 149·5°. It is reduced by hydrogen in the presence of platinum black to p-*aminobenzoyl*-N-*dimethyl-leucinol hydrochloride*, bright yellow needles, m. p. 196°. N-*Diethyl-leucine ethyl* ester is prepared by condensing racemic α-bromo-*iso*hexoic acid with diethylamine and esterifying; it forms a pale yellow oil, b. p. 204—208°/720 mm. It is reduced by sodium and alcohol to N-*diethyl-leucinol*, a colourless oil, b. p. 208—211°. p-*Nitrobenzoyl*-N-*diethyl-leucinol hydrochloride* forms pale yellow needles, m. p. about 163° (depending on the rate of heating). p-*Aminobenzoyl*-N-*diethyl-leucinol hydrochloride* forms white leaflets, m. p. 191°. N-*Pentamethyleneleucine ethyl* ester [*ethyl* α-*piperidino-isohexoate*], from α-bromo*iso*hexoic acid and piperidine, forms an oil, b. p. 248—255°/726 mm.; by reduction, it gives N-*pentamethyleneleucinol* [β-*piperidinoisohexyl alcohol*], b. p. 250—252°. The p-*nitrobenzoate hydrochloride* crystallises in nodular aggregates of thin prisms, m. p. 156°, and the p-*aminobenzoate hydrochloride* crystallises similarly.

The synthesis of 3 : 4-methylenedihydroxyphenylalaninecholine iodide was accomplished as follows. *Piperonyl bromide* was obtained by the action of hydrogen bromide on piperonyl alcohol; it crystallises in needles, and does not form a compound with magnesium in ether solution. It condenses with ethyl malonate, by means of sodium in alcoholic solution, forming *ethyl piperonylmalonate*, $CH_2{:}O_2{:}C_6H_3 \cdot CH_2 \cdot CH(CO_2Et)_2$, a yellow, viscous oil, b. p. 200—220°/15 mm., which when hydrolysed gives piperonylmalonic acid, m. p. 156°. This was brominated to *bromopiperonylmalonic* acid, $CH_2{:}O_2 \cdot C_6H_3 \cdot CH_2 \cdot CB(CO_2Et)_2$, m. p. 147—148° (decomp.), which when heated at 120—130° loses carbon dioxide, forming *α-bromopiperonylacetic acid*. The latter was not isolated, but was heated directly with dimethylamine at 100°; the N-*dimethyl*-3 : 4-*methylenedioxyphenylalanine* formed was not isolated but treated with alcohol and hydrochloric acid, forming the *ethyl* ester, a viscous, yellow oil, b. p. 200°/14 mm. This was reduced with sodium and alcohol forming N-*dimethyl*-3 : 4-*methylenedioxyphenylalaninol*,

$$CH_2{:}O_2{:}C_6H_3 \cdot CH_2 \cdot CH(NMe_2) \cdot CH_2 \cdot OH,$$

b. p. 180°/14 mm.; the *hydrochloride* crystallises in white leaflets, m. p. 165°. When the alaninol is treated with excess of methyl iodide in alcohol solution, 3 : 4-*methylenedioxyphenylalaninecholine iodide* [β-*dimethylamino*-γ-*piperonylpropyl alcohol methiodide*], m. p. 184°, is formed. The following palmitic and stearic

acid esters of proteinogenous cholines are described: p-*methoxyphenylalanine methiodide stearate*, bunches of needles, sinters from 98°, m. p. 195°; the corresponding *palmitate*, similar crystals, m. p. 138—141°; *alanine methiodide stearate*, silky leaflets, m. p. 210—212°; *palmitate*, white needles, m. p. 203—210°; *alanine methochloride stearate*, hygroscopic needles, m. p. 202—205°, and *palmitate*, m. p. 202—205°. E. H. R.

Effect of Silver Nitrate and Alkali Nitrates on Aromatic Anhydrides. C. V. GHEORGHIU (*Ann. Sci. Univ. Jassy*, 1923, ii, 308—309; from *Chem. Zentr.*, 1923, iii, 1155).—Benzoic anhydride when heated with silver nitrate explodes with evolution of gas, development of the odour of nitrobenzene, and formation of silver. Phthalic anhydride and coumarin behave in a similar way. The alkali nitrates can also act like silver nitrate. The author supposes that benzoyl peroxide or perbenzoic acid, the salts of which are explosive, may be formed, *e.g.*, $4Bz_2O+2NaNO_3=2BzONa+3Bz_2O_2+N_2$. For the per-acids the formulæ

$CO_2H\cdot C_6H_4\cdot CO\cdot O\cdot OH$ and $OH\cdot C_6H_4\cdot CH{:}CH\cdot CO\cdot O\cdot OH$,

respectively, are given. Nitrobenzene is probably formed by nitration of benzoyl peroxide. G. W. R.

***o*-Nitrophenylpropionic Acid.** A. JAENISCH (*Ber.*, 1923, **56**, [*B*], 2448—2450).—An improved method is described for the conversion of *o*-nitrobenzylmalonic ester into β-*o*-nitrophenylpropionic acid, m. p. 115°; the *silver*, *lead*, *copper*, *mercury*, *barium*, *calcium* (+$2H_2O$), and *zinc* (+$2H_2O$) salts are described. The *methyl* ester is a liquid, b. p. 171—172°/12 mm. β-*o*-*Nitrophenylpropionyl chloride*, needles, m. p. 43° (prepared from the acid and phosphorus pentachloride) is transformed by ammonia into the corresponding *amide*, colourless plates and needles, m. p. 121—122°, which is converted by Hofmann's method into the *bromoamide*, $C_8H_9O_3N_2Br$, yellow needles, m. p. 136—137°, and thence into β-*o*-*nitrophenylethylamine*, $NO_2\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NH_2$, a liquid, b. p. 147°/13 mm. (*hydrochloride*, plates, m. p. 174·5°; picrate, m. p. 148·5°). *Benzo*-β-*o*-*nitrophenylethylamide*,

$NO_2\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NHBz$,

crystallises in stellar aggregates, m. p. 98°; it is reduced by phosphorus and hydriodic acid to *benzo*-β-*o*-*aminophenylethylamide*, leaflets, m. p. 135° (the *hydriodide* is described). β-*o*-*Nitrophenylethylphthalimide*, $NO_2\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot N{:}C_8H_4O_2$, needles, m. p. 120—121°, β-*o*-*aminophenylethylphthalimide*, needles, m. p. 163°, β-*o*-*nitrophenylethylsuccinimide*, needles, m. p. 116°, and β-*o*-*aminophenylethylsuccinimide*, needles, m. p. 141°, are described. Reduction of β-*o*-nitrophenylethylamine by phosphorus and hydriodic acid yields β-*o*-aminophenylethylamine [*di-hydroiodide*, yellow needles and leaflets, m. p. (indefinite) 260°; *dihydrochloride*, softening at 184°; *picrate*, m. p. 142—143°; *benzoyl* derivative, m. p. 139—140°].

ω-*o*-*Nitrobenzylacetophenone*, stellar aggregates, m. p. 68—69°, prepared from *o*-nitrobenzylacetyl chloride, benzene, and aluminium chloride is reduced by phosphorus and hydriodic acid to 2-phenyl-

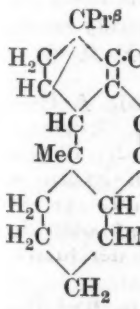
quinoline, m. p. 81°. *α-Keto-γ-o-nitrophenyl-α-anisylpropane*, pale yellow rodlets, m. p. 59°, and *2-anisylquinoline*, leaflets, m. p. 123·5°, are described. Similarly, the reduction of *ethyl o-nitrobenzylmethylacetoacetate*, a liquid, yields 2 : 3-dimethylquinoline, m. p. 64·5°, and not a dihydro-derivative.

β-o-Nitrophenylpropionitrile, prepared from the amide and thionyl chloride, m. p. 41—42°, is reduced by stannous chloride and hydrochloric acid to 2-aminoquinoline hydrochloride.

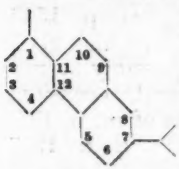
α-Bromo-β-o-nitrophenylpropionic acid, rhombohedra, m. p. 115—116°, is prepared by the action of bromine and phosphorus on the parent acid or by heating *bromo-o-nitrobenzylmalonic acid*, prisms, m. p. 143° (decomp.). *α-Hydroxy-β-o-nitrophenylpropionic acid*, rectangular plates, m. p. 103°, is prepared from the bromo-acid and silver nitrate solution; it is decomposed by sodium hydroxide solution with production of *o*-nitrotoluene. H. W.

ααβ-Triphenylpropionic Acid and some of its Derivatives. [Mme] P. Ramart (*Compt. rend.*, 1924, **178**, 93—96).—*Benzyl diphenylacetate* (needles, m. p. 35°, b. p. 205—207°/2 mm.), from diphenylacetyl chloride and benzyl alcohol, when treated successively with sodamide and benzyl chloride, affords *benzyl ααβ-triphenylpropionate* (prisms, m. p. 85°, b. p. 270—275°/2 mm.). The latter, on hydrolysis, affords *ααβ-triphenylpropionic* acid (prisms, m. p. 132°; *amide*, needles, m. p. 111°). The nitrile (m. p. 126°) is formed from benzyl chloride and sodio-diphenylacetonitrile, or from phosphoric oxide and the amide (above). Neure (A., 1889, 597) obtained the nitrile, but was mistaken with regard to the constitution of his acid of m. p. 162° (cf. Bistrzycki and Mauron, A., 1910, i, 845). E. E. T.

Higher Terpene Compounds. XVI. The Carbon Framework of Abietic Acid and Dehydrogenating Disruption in the Abietic Acid Series. L. Ruzicka, H. Schinz, and J. Meyer (*Helv. Chim. Acta*, 1923, **6**, 1077—1096).—The annexed constitutional formula for abietic acid (pinabietic acid) put forward by Virtanen (A., 1921, i, 669) does not conform with the principle, which has been found general for the sesquiterpenes, that the carbon framework must be divisible into isoprene residues. This formula was based partly on the observation that the hydrocarbon abietin, $C_{19}H_{28}$, when oxidised with manganese dioxide and sulphuric acid, gives trimellitic acid. Hence it is argued that abietin must contain a benzene ring and that the corresponding ring in abietic acid must contain the double bond and the bridge-ring (or, as is now known to be the case, the two double bonds) as well as the carboxyl group. A study of the oxidation of abietin, abietene, methylabietin, and abietic acid leads to the conclusion that Virtanen's reasoning is incorrect. Methylabietin, which, according to Virtanen, should also contain a benzene ring, is com-



pletely oxidised by cold aqueous permanganate to acids, and by oxidation with manganese dioxide and sulphuric acid it gives trimellitic acid, as also does abietic acid. It is concluded, therefore, that the carboxyl group cannot be in the same ring as the *iso*propyl group, and as the 9 and 10 positions are excluded (see annexed diagram and A., 1922, i, 829), the only remaining positions are 2, 3, and 4. The remaining methyl group may be in position 11, or possibly in 12, but only if the carboxyl is in 2.



Oxidation of abietic acid and its related compounds with manganese dioxide and 57% sulphuric acid leads to a mixture of benzene polycarboxylic acids, some of which are formed normally from the carbon framework of the oxidised substance, some indirectly. Trimellitic acid and mellophanic acid (which is confirmed to be the 1 : 2 : 3 : 4-tetracarboxylic acid, cf. Bamford and Simon, T., 1910, **97**, 1904) are probably formed normally, and are obtained from abietene (mixed with abietin), abietic acid, and methylabietin. Pyromellitic acid and benzenepentacarboxylic acid are obtained from abietic acid, their formation being possibly due to polymerisation of the abietic acid at a double bond. A number of methods in which this may occur are discussed. Retenequinone and methylretenequinone are oxidised to mellitic acid, whilst the former also gives pyromellitic acid. Dihydroabietene is oxidised to mellophanic acid without formation of any trimellitic acid, and the same is the case when methylabietin is oxidised first with cold permanganate and then boiled with manganese dioxide and sulphuric acid.

The mechanism of the oxidation of the above compounds with manganese dioxide and sulphuric acid consists first in dehydrogenation of the individual hydroaromatic rings followed by disruption to benzenecarboxylic acids. The process is referred to as "dehydrogenating disruption." The different benzenepolycarboxylic acids are best separated by fractional distillation of their methyl esters, which crystallise readily.

The reduction of ethyl abietate by Bouveault's method to abietenol, which still contains one unsaturated bond, indicates that there is no double bond in the ring containing the carboxyl group (A., 1922, i, 829). The exact position of the double bonds in abietic acid remains uncertain. E. H. R.

Higher Terpene Compounds. XVII. The Gentle Action of Potassium Permanganate on Abietic Acid. L. Ruzicka and J. Meyer (*Helv. Chim. Acta*, 1923, **6**, 1097—1108).—To obtain a crystalline product by the oxidation of abietic acid with potassium permanganate, great care is required. The oxidation is carried out in potassium hydroxide solution, using 2 to 3 atoms of available oxygen per mol., and at a high dilution. After fifteen hours, the manganese dioxide is filtered off and unoxidised abietic acid precipitated by a current of carbon dioxide. When part of the oxidation product has started to precipitate, the solution is filtered and the main product precipitated with acetic acid. The precipi-

tate is filtered, dried, and digested with a little methyl alcohol, which leaves a crystalline residue, about 3—8% of the weight of the abietic acid taken, m. p. 106°. This is separable by fractional precipitation into an unknown *substance*, $C_{18}H_{32}O_7$, m. p. 154°, and a *dihydroxyabietic acid*, $C_{20}H_{30}O_2(OH)_2$, m. p. 152°, which gives a *diacetyl* derivative, m. p. 163° (decomp.), and a possibly stereoisomeric diacetyl compound, m. p. 240°. On separate occasions the oxidation took different courses, giving products of m. p. 135° and 360°. E. H. R.

The Resolution of *dl*-Tyrosine into its Two Optically Active Components. E. ABDERHALDEN and H. SICKEL (*Z. physiol. Chem.*, 1923, **131**, 277—280).—Formyl-*dl*-tyrosine, obtained from tyrosine by boiling with formic acid for three hours, has been separated into its components by recrystallisation from hot water containing four equivalents of brucine. The *brucine* salt of formyl-*d*-tyrosine which crystallises out forms four- or six-sided leaflets, which decompose at 145°. Formyl-*d*-tyrosine is obtained from this salt on decomposing it with alkali. Hydrolysis of formyl-*d*-tyrosine with 10% hydrochloric acid yields *d*-tyrosine, $[\alpha]_D^{23}$ +8·7°. The corresponding *l*-salt was not obtained pure from the mother-liquors. The best preparation gave $[\alpha]_D^{23}$ −6·2°. W. O. K.

Dichlorotyrosine [α-Amino-β-3 : 5-dichloro-4-hydroxyphenylpropionic Acid]. CHEMISCHE FABRIK FLORA (Swiss Pat. 99453; from *Chem. Zentr.*, 1923, iv, 828).—A suspension of tyrosine in acetic acid is treated with chlorine. *Dichlorotyrosine hydrochloride* separates out from which the free *base* may be obtained in crystalline form. It is optically active. G. W. R.

Preparation of Dibromotyrosine [α-Amino-β-3 : 5-dibromo-4-hydroxyphenylpropionic Acid]. CHEMISCHE FABRIK FLORA (Swiss Pat. 95300; from *Chem. Zentr.*, 1923, iv, 663).—A suspension of tyrosine in acetic acid is treated with bromine; from the products of reaction, *α-amino-β-3 : 5-dibromo-4-hydroxyphenylpropionic* acid is obtained. It is crystalline and optically active. G. W. R.

Derivatives of α-Naphthol-2-carboxylic Acid. SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (D.R.-P. 373736; from *Chem. Zentr.*, 1923, iv, 593).—Additional to Brit. Pat. 195513. *4 : 4′-Dihydroxydinaphthylketone-3 : 3′-dicarboxylic acid* is a powder decomposing at 259°. *α-Naphthol-2 : 4-dicarboxylic acid* decomposes at about 286°. G. W. R.

α-Naphthol-4-carboxylanilide. SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pat. 99280; from *Chem. Zentr.*, 1923, iv, 829).—An ester of α-naphthol-4-carboxylic acid, for example, methyl α-naphthol-4-carboxylate, is heated with aniline. *α-Naphthol-4-carboxylanilide* thus obtained is crystalline and has m. p. 203° G. W. R.

The Constitution of Sparassol. E. WEDEKIND and K. FLEISCHER (*Ber.*, 1923, **56**, [*B*], 2556—2563; cf. Falck, *ibid.*, 2555).—The substance is shown to be methyl 4-hydroxy-2-methoxy-*o*-toluate.

Sparassol, $C_{10}H_{12}O_4$, crystallises from methyl or ethyl alcohol in needles, m. p. 67—68°. It contains two methoxyl groups, is saturated, and does not possess a ketonic or a reactive methylene group. Its aromatic nature is established by the isolation of *methyl* 3(?5)-*nitro*-4-*hydroxy*-2-*methoxy*-o-*toluate*, yellow needles, m. p. 168—169°, and *methyl* 3 : 5-*dinitro*-4-*hydroxy*-2-*methoxy*-o-*toluate*, small, pale yellow needles, m. p. 150°. The presence of a phenolic hydroxyl group in sparassol is established by its solubility in alkali hydroxide, but not in alkali carbonate, and by the formation of *methyl* 4-*acetoxy*-2-*methoxy*-o-*toluate*, small, hexagonal plates, m. p. 63—64°, and of *methyl* 2 : 4-*dimethoxy*-o-*toluate*, rhombic plates, m. p. 42—43·5°; the isolation of 4-*hydroxy*-2-*methoxy*-o-*toluic acid*, m. p. 165—166° (decomp.) after slight previous softening, as by-product of the action of methyl sulphate and potassium hydroxide on sparassol indicates the presence of the carbomethoxy-group. When treated with fuming hydrochloric acid under pressure, sparassol yields orcinol. A comparison of the properties of sparassol and the corresponding carboxylic acid with those of the known orcinolcarboxylic acids and their methylated derivatives excludes the possibility that the constitution of sparassol is other than methyl 4-hydroxy-2-methoxy-*o*-toluate.

It is established that the amount of benzenoid compounds in the culture medium is insufficient to account for the production of sparassol; an example is therefore afforded of the conversion of an aliphatic compound (sugar) into an aromatic substance by a biochemical method. H. W.

Preparation of Aryl Hydroxynaphthyl Ketones. SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (D.R.-P. 378908, 378909, and Swiss Pat. 98559; from *Chem. Zentr.*, 1923, iv, 593—594).—β-Naphthol or negatively substituted derivatives of α- or β-naphthol are treated with aryl trichlorides with or without addition of diluents or condensing reagents in the absence of alkali hydroxides. The carboxylic acids and sulphonic acids of 4-hydroxynaphthalene-1-arylketens are heated at high temperatures, preferably in suspension or in the presence of diluents. 1-Hydroxynaphthalene-2-carboxylic acid when heated with benzotrichloride at 100—120° until evolution of hydrogen chloride has ceased, or at 15° in the presence of strong sulphuric acid, gives 4-*hydroxy*-1-*benzoylnaphthalene*-3-*carboxylic acid*, small needles, m. p. 205°. On heating the latter compound under pressure with strong sulphuric acid, phenyl 4-hydroxy-α-naphthyl ketone is obtained, m. p. 164—165°. 4-*Hydroxy*-1-o-*chlorobenzoylnaphthalene*-3-*carboxylic acid*, from 1-hydroxynaphthalene-2-carboxylic acid and *o*-chlorobenzotrichloride, has m. p. 213°. 1-*Chloro*-4′-*hydroxy*-2 : 1′-*dinaphthyl-ketone*-3′-*carboxylic acid*, from 1-hydroxynaphthalene-2-carboxylic acid and 1-chloro-2-naphthotrichloride, has m. p. 210—211°. The following com-

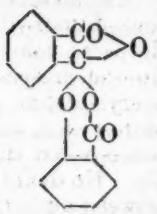
pounds are also mentioned: *phenyl 2-hydroxy-α-naphthyl ketone*, m. p. 175°, from β-naphthol and benzotrichloride; *2-hydroxy-1-benzoylnaphthalene-3-carboxylic acid*, from 2-hydroxynaphthalene-3-carboxylic acid and benzotrichloride; *phenyl 5-chloro-4-hydroxy-α-naphthyl ketone*, m. p. 121°, from 8-chloro-1-hydroxynaphthalene and benzotrichloride; *4-hydroxy-1-benzoylnaphthalene-3-sulphonic acid*, a white powder giving phenyl 4-hydroxy-α-naphthyl ketone by elimination of the sulphonic acid group, from 1-hydroxynaphthalene-2-sulphonic acid and benzotrichloride; *4-hydroxy-1-benzoylnaphthalene-5-sulphonic acid*; *1-hydroxy-2-benzoylnaphthalene-4-sulphonic acid*; *1-hydroxy-2-benzoylnaphthalene-5-sulphonic acid*. By heating the above-mentioned carboxylic acids or sulphonic acids with 5% sulphuric acid under pressure at 180—190°, or in the presence of dimethylaniline at 150°, the carboxylic acid or sulphonic acid groups are eliminated. Examples are given of the preparation by this reaction of *phenyl 4-hydroxy-α-naphthyl ketone*, *1-chloro-4'-hydroxy-2 : 1'-dinaphthyl ketone*, crystals, m. p. 213°, and *4 : 4'-dihydroxy-1 : 1'-dinaphthyl ketone*. G. W. R.

3-Methoxynaphthalene-2-ketocarboxylic Acid. W. Dilthey and G. Lipps (*Ber.*, 1923, **56**, [*B*], 2443—2445).—3-Acetyl-2-methoxynaphthalene condenses with benzaldehyde in the presence of alcoholic sodium ethoxide to give *2-cinnamoyl-3-methoxynaphthalene*, $C_6H_4<\begin{matrix}CH{:}C\cdot OMe\\ CH{:}C\cdot CO\cdot CH{:}CHPh\end{matrix}$, deep yellow leaflets, m. p. 87°, which is oxidised by potassium permanganate in the presence of pyridine to *3-methoxy-2-naphthoylformic acid*, $C_6H_4<\begin{matrix}CH{:}C\cdot OMe\\ CH{:}C\cdot CO\cdot CO_2H\end{matrix}$, pale greenish-yellow crystals, m. p. 162—163° (decomp.). The presence of the carbonyl group in the latter acid could not be established in the usual manner, but it is shown that the gas evolved when it is melted consists of approximately equal volumes of carbon monoxide and carbon dioxide. Attempts to oxidise it to 3-methoxynaphthalene-2-carboxylic acid were unsuccessful, the substance being either unchanged or transformed into β-naphthyl methyl ether. During the preparation of the acid, a second acid, colourless, rhombohedral crystals, m. p. 142—143°, is also obtained, the constitution of which has not been elucidated.

The following substances are also described: *1-cinnamoyl-4-ethoxynaphthalene*, yellow needles or almost colourless leaflets, m. p. 85°; *2-methoxycinnamoyl-3-methoxynaphthalene*, yellow needles, m. p. 99—100°; *1-methoxycinnamoyl-4-ethoxynaphthalene*, greenish-yellow needles, m. p. 110—111°; *2-o-chlorocinnamoyl-3-methoxynaphthalene*, pale yellow needles, m. p. 121°; *1-o-chlorocinnamoyl-4-ethoxynaphthalene*, pale yellow needles, m. p. 97—98°. H. W.

Substituted Salicylic Acids. III. The Reaction of γ-Dicarboxyl Chlorides with Sodium Salicylate. H. P. Kaufmann and H. Voss (*Ber.*, 1923, **56**, [*B*], 2508—2514; cf. A., 1922, i, 252; 1923, i, 795).—The condensation of *s-o*-phthaloyl chloride with sodium or disodium salicylate with the production of salicylic

phthalidylidene ether ester (annexed formula) has caused the authors to examine the action with other γ-dicarboxyl chlorides. The problem is intimately connected with the transformation of symmetrical into unsymmetrical acid chlorides and the production of unsymmetrically constituted derivatives from the former.

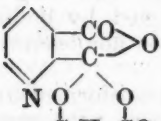


s-Tetrachlorophthaloyl chloride reacts with disodium salicylate in the presence of benzene to give *salicylic tetrachlorophthalidylidene ether* ester, colourless crystals, m. p. 199°, which is stable towards cold sodium carbonate solution, but is hydrolysed when warmed. as-*Tetrachlorophthaloyl chloride*, prepared by the action of aluminium chloride on the symmetrical chloride at 150° (cf. Ott, A., 1912, i, 828) long, lustrous needles, m. p. 137°, is more stable than *as*-phthaloyl chloride, and is only partly transformed into the symmetrical variety when distilled.

s-$\Delta^{2:6}$-*Dihydrophthaloyl chloride*, a pale yellow liquid, b. p. 122°/13 mm., gives with sodium salicylate in the presence of ether *salicylic* $\Delta^{2:6}$-*dihydrophthalidylidene ether* ester, colourless crystals, m. p. 165°; as-$\Delta^{2:6}$-*dihydrophthaloyl chloride* forms pale yellow crystals, m. p. 131°.

s-Δ^{2}-*Tetrahydrophthaloyl chloride*, a pale yellow liquid, b. p. 129°/14 mm., is readily converted into *salicylic* Δ^{2}-*tetrahydrophthalidylidene ether* ester, a colourless substance, m. p. (indefinite) 105° (decomp.). The conversion of the symmetrical into the unsymmetrical chloride could not be effected.

Pyridine-2 : 3-dicarboxyl chloride and sodium salicylate in the presence of boiling benzene give *salicylic pyridinephthalylidylidene ether* ester (annexed formula), m. p. 168°.



Succinyl chloride and sodium salicylate yield *salicylic succinidylidene ether* ester which exists in two isomeric forms, colourless needles, m. p. 176° when rapidly heated, and m. p. 192°; the former compound passes into the latter when it is boiled with glacial acetic acid. The isomerism probably depends on keto-enolic desmotropy.

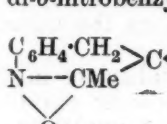
Salicylic maleinidylidene ether ester, m. p. 204°, is prepared with the aid of fumaroyl chloride. It dissolves in cold sodium carbonate solution, from which it is precipitated unchanged by acetic acid. The unusual solubility is attributed to the wandering of a hydrogen atom, although the mobility of hydrogen attached to a doubly bound carbon atom is surprising.

[With W. Dähnert.]—αβ-Dibromomaleinyl chloride reacts with sodium salicylate in the presence of ether to give *salicylic αβ-dibromomaleinidylidene ether* ester, needles, m. p. 160°, which does not dissolve in cold sodium carbonate solution. H. W.

The Diphenic Acid and the Fluorenone Series. I. H. W. Underwood, jun., and E. L. Kochmann (*J. Amer. Chem. Soc.*, 1923, **45**, 3071—3077).—Diphenic anhydride and phenol react in the

presence of fuming stannic chloride and from the product phenoldiphenein, colourless, rhombic crystals, m. p. 250—251°, and an amorphous powder were isolated. The former dissolved in sodium hydroxide to a yellow solution, whilst the latter gave a deep red colour. The reaction between resorcinol and the anhydride in the presence of zinc chloride gave resorcinol-diphenein, colourless crystals, m. p. 178—179°, soluble in sodium hydroxide without fluorescence, and an amorphous powder which gave strong fluorescence when dissolved in dilute sodium hydroxide (T., 1923, **123**, 225). No definite substance was isolated from the product of reaction between diphenic anhydride and pyrogallol in the presence of stannic chloride. Diphenic anhydride was converted into its isomeride diphenyleneketone-4-carboxylic acid on heating with stannous chloride or zinc chloride, and the reverse change was accomplished by heating the ketone acid with acetic anhydride and glacial acetic acid. The ketone acid reacted with phenol and resorcinol to give amorphous substances identical with those obtained in the reactions described above. Fluorenone reacted with phenol and resorcinol to give similar products. None of these products appear to possess quinoid structure. F. B.

Certain Cyclic and Fatty-aromatic Bases from Di-*o*-nitrobenzyl-acetoacetic and -malonic Esters. S. GABRIEL and REINHOLD WOLTER (*Ber.*, 1923, **56**, [*B*], 2445—2448).—Ethyl di-*o*-nitrobenzylacetoacetate is reduced by stannous chloride in the presence of glacial acetic and fuming hydrochloric acids to the *substance* (annexed formula), colourless needles, m. p. 184° after softening at 178°, which is transformed by boiling hydriodic acid into non-homogeneous 3-*o*-aminobenzyl-2-methylquinoline (see below).



Ethyl di-*o*-nitrobenzylmalonate is conveniently transformed into di-*o*-nitrobenzylacetic acid, m. p. 149°, by treatment with somewhat diluted sulphuric acid at 180—185°. *Di-o-nitrobenzylacetyl chloride*, prepared from the acid and phosphorus pentachloride, m. p. 91—92°, is converted by ethyl sodiomalonate in the presence of benzene into *ethyl di-o-nitrobenzylacetylmalonate*,

$$(NO_2\cdot C_6H_4\cdot CH_2)_2CH\cdot CO\cdot CH(CO_2Et)_2,$$

colourless, rhombic leaflets, m. p. 80° after softening at 77°, from which *di-o-nitrobenzylacetone*, $(NO_2\cdot C_6H_4\cdot CH)_2CH\cdot COMe$, prisms, m. p. 89—89·5°, is prepared by the action of boiling hydrochloric acid. The ketone is reduced by phosphorus and hydriodic acid to 3-*o*-*aminobenzyl-2-methylquinoline* (see above), flat needles or oblong plates, m. p. 166—167°, which yields a crystalline *dihydroiodide* and *dihydrochloride*. The base is converted by phthalic anhydride into the *substance*, $C_{25}H_{18}O_2N_2$, m. p. 127—128°, and by benzaldehyde into the *benzylidene* derivative, m. p. 170—171°. Di-*o*-nitrobenzylacetylchloride is converted by benzene and aluminium chloride into *di-o-nitrobenzylacetophenone*,

$$(NO_2\cdot C_6H_4\cdot CH_2)_2CH\cdot COPh,$$

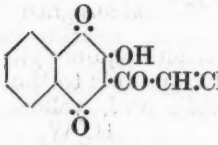
m. p. 108—108·5°, which is transformed by hydriodic acid and phosphorus into 2-*phenyl*-3-o-*aminobenzylquinoline*, m. p. 177—178°; the base yields the *compound* $C_{30}H_{20}O_2N_2$, m. p. 185°, when treated with phthalic anhydride.

Di-o-*nitrobenzylacetamide*, colourless leaflets, m. p. 162°, prepared by the action of ammonia on a concentrated solution of the corresponding chloride in benzene, could not be transformed into the amine by potassium hypobromite. It is converted, however, by the action of sodium and bromine in the presence of alcohol into the *compound* $(NO_2\cdot C_6H_4\cdot CH_2)_2CH\cdot NH\cdot CO_2Me$, needles, m. p. 139°, which is hydrolysed and decomposed by sulphuric acid at 120° into *di*-o-*nitrobenzylmethylamine*,

$$(NO_2\cdot C_6H_4\cdot CH_2)_2CH\cdot NH_2,$$

colourless, hexagonal plates, m. p. 82—83° (the *sulphate* is described). Treatment with red phosphorus and hydriodic acid converts the base into *di*-o-*aminobenzylmethylamine*, a glassy solid which yields a *trihydroiodide*, decomp. above 230°, and a *trihydrochloride* which softens above 260°. H. W.

The Action of Potassium Ferricyanide on Quinizarin in Alkaline Solution. R. Scholl, P. Dahll, and F. Hansgirg (*Ber.*, 1923, **56**, [*B*], 2548—2555).—The oxidation of 1 : 4-dihydroxyanthraquinone by potassium ferricyanide in alkaline solution occurs in a similar manner to that of alizarin (Scholl and Zinke, A., 1919, i, 25, 406) and leads to the formation of β-2-hydroxy-1 : 4-naphthaquinonyl-3-acrylic acid (annexed formula).



[With P. Hasenclever and F. Fleischmann.]—A solution of 1 : 4-dihydroxyanthraquinone in aqueous potassium hydroxide is rapidly oxidised by six molecular proportions of potassium ferricyanide to β-2-*hydroxy*-1 : 4-*naphthaquinonoyl*-3-*acrylic acid*, yellow needles; the acid decomposes rapidly at about 190°, and more slowly at a lower temperature even in solution. The *ammonium* salt, the *potassium* salt, $C_{14}H_6O_6K_2$, and the *silver* salt, $C_{14}H_6O_6Ag_2$, are described. The silver salt is converted by methyl iodide at the atmospheric temperature in the absence of light into *methyl* β-2-*hydroxy*-1 : 4-*naphthaquinonyl*-3-*acrylate*,

$$OH\cdot C_{10}H_4O_2\cdot CO\cdot CH:CH\cdot CO_2Me,$$

greenish-yellow, crystalline needles, m. p. 158°, the *sodium* salt of which is described. The acid is converted by saturated methyl-alcoholic hydrogen chloride into β-2-*methoxy*-1 : 4-*naphthaquinonyl*-3-*acrylic acid*, m. p. 165°, which is transformed by aqueous sodium acetate into the orange-yellow *sodium* salt; the *silver* salt, a yellow, amorphous substance, is also described. The esterification of the naphtholic hydroxyl group by alcoholic hydrogen chloride has been observed previously, but it is very remarkable that the carboxyl group remains unaffected; the possibility that the product is a lactone, $OMe\cdot C_{10}H_4O_2\cdot C(OH)\cdot CH:CH\cdot CO$ (O bridge), cannot therefore be

disregarded. The phenolic ester, m. p. 158°, is isomerised by treatment with methyl-alcoholic hydrogen chloride to the methoxy-acid, m. p. 165°. *Methyl* β-2-*methoxy*-1 : 4-*naphthaquinonyl*-3-*acrylate*, $OMe{\cdot}C_{10}H_4O_2{\cdot}CO{\cdot}CH{:}CH{\cdot}CO_2Me,MeOH$, pale yellow needles, m. p. 130—131° (decomp.), is prepared by the action of a large excess of boiling methyl iodide on the di-silver salt of the hydroxy-acid; the firmness with which the molecule of methyl alcohol is retained suggests that it is attached to a carbonyl group in the form of a semi-acetal. The hydroxy- and methoxy-acids are only very slowly acted on by bromine dissolved in chloroform, whereas the phenolic ester, m. p. 158°, absorbs two atomic proportions of the halogen, one of which is subsequently lost in the form of hydrogen bromide. The hydroxy-acid and the phenolic ester give reddish-brown or orange-yellow solutions in hot sodium hydroxide solution, which rapidly become dark blue and from which a dark violet acid is precipitated by dilute sulphuric acid; this acid has not been obtained in the homogeneous crystalline form, but there can be little doubt that it is a chromanone derivative, $C_6H_4<\begin{matrix}CO{\cdot}C\text{—}O{\cdot}CH{\cdot}CO_2H\\ CO{\cdot}C{\cdot}CO{\cdot}CH_2\end{matrix}$. The phenolic ester, unlike the hydroxy- or methoxy-acid, is converted rapidly at the atmospheric temperature by ammonia into a bluish-black compound, to which the constitution $C_6H_4<\begin{matrix}CO{\cdot}C{\cdot}NH{\cdot}CH{\cdot}CO_2Me\\ CO{\cdot}C{\cdot}CO\text{—}CH_2\end{matrix}$ is assigned.

Reduction of di-potassium β-2-hydroxy-1 : 4-naphthaquinonyl-3-acrylate by sodium hyposulphite in aqueous solution leads to the production of β-1 : 2 : 4-*trihydroxy*-3-*naphthoylacrylic acid*, yellow needles, m. p. 208°. H. W.

Bile Acids. X. M. Schenck (*Z. physiol. Chem.*, 1923, **131**, 269—276).—(1) Deoxycholic acid, when heated with alcoholic ammonia in a sealed tube at about 220° yields the amide, $C_{24}H_{41}O_3N$, m. p. 186°, which crystallises from a mixture of alcohol and water in needles containing $3H_2O$. (2) Biloidanic acid, obtained from bilianic acid purified by means of a new method through the dioxime, has the formula $C_{22}H_{32}O_{12}$. From *iso*bilianic acid, when oxidised by 32—35% nitric acid, there is obtained in small yield a *triketotricarboxylic acid*, $C_{24}H_{32}O_9$, fine, six-sided, rectilinear plates which froth and turn brown at 230—235°. W. O. K.

Preparation of Deoxycholic Acid. J. D. Riedel, Akt.-Ges (D.R.-P. 374367; from *Chem. Zentr.*, 1923, iv, 726).—Dihydroxycholenic acid is hydrogenated in the presence of catalysts. Deoxycholic acid is obtained from the products by way of the crystalline acetic acid–deoxycholic acid compound, m. p. 141°. G. W. R.

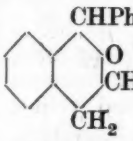
Preparation of an Unsaturated Bile Acid. J. D. Riedel, Akt.-Ges. (D.R.-P. 374366; from *Chem. Zentr.*, 1923; iii, 726; cf. A., 1922, i, 1160).—In variation of an earlier patent, dihydroxycholenic acid, m. p. 260°, is treated with bromine and alkaline

reagents. For example, dihydroxycholenic acid is treated with bromine in methyl-alcoholic solution. From the products, after boiling with an alkali hydroxide, a substance, apparently *dihydroxycholadienic acid*, is obtained, m. p. 245—247°. G. W. R.

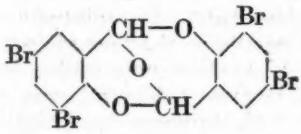
Preparation of Benzaldehyde. THE BARRETT CO. (Brit. Pat. 189091).—The catalytic action of the oxides of various metals on toluene, in the vapour phase and in the presence of a gas containing oxygen (*e.g.*, air, oxygen, ozone), is found to differ considerably. Thus, vanadium oxide gives benzoic acid, benzaldehyde, maleic acid, and a measurable amount of the products of complete combustion; the oxides of molybdenum, tantalum, tungsten, and zirconium give relatively high yields of benzaldehyde and a relatively low degree of combustion; the oxides of uranium, manganese, copper, nickel, chromium, and thorium give relatively high yields of benzaldehyde together with relatively high degrees of combustion; the oxides of cobalt and cerium give relatively low yields of benzaldehyde and relatively high degrees of combustion, whilst the oxides of titanium, bismuth, and tin give relatively low yields of benzaldehyde and relatively low degrees of combustion. Greatly increased yields of benzaldehyde, accompanied by low degrees of combustion, are obtained by using as catalyst mixtures of the above oxides, provided that at least one of these oxides is that of a metal of the fifth or sixth periodic group. Particularly efficient is a mixture of oxides of uranium and molybdenum (approximately in the proportion of from three to thirteen of the former to one of the latter), or of oxides of molybdenum, uranium, and copper. In preparing these oxides, the best results are obtained by starting from a solution of the metals in organic acids. The temperature of the catalyst should be between about 300° and 700°. W. T. K. B.

Organomagnesium Derivatives. III. A. GARCÍA BANÚS and L. MEDRANO (*Anal. Fís. Quím.*, 1923, **21**, 436—463; cf. García Banús and Vila, A., 1922, i, 734).—A study of the reaction between benzaldehyde and magnesium benzyl halides. On adding benzaldehyde (1 mol.) to magnesium benzyl iodide (1 mol.) in ethereal solution, the reaction proceeds normally, yielding phenyl-*o*-tolylcarbinol, whilst, when magnesium benzyl bromide is used, phenylbenzylcarbinol, crystals, m. p. 62—65°, is formed. In the inverse reaction, where magnesium benzyl bromide is added to benzaldehyde in ethereal solution, stilbene, phenylbenzylcarbinol, and diphenyl-*iso*chroman, m. p. 90—95°, are formed. Using an excess of benzaldehyde with magnesium benzyl chloride, phenylbenzylcarbinol is formed by reaction in the cold. When the reaction is carried out with boiling in a reflux apparatus, the reaction proceeds differently. From the products of the reaction, dibenzoylphenylmethane, m. p. 144—146°, stilbene, deoxybenzoin, benzylidenedeoxybenzoin, m. p. 101—102°, and *iso*benzylidenedeoxybenzoin, m. p. 86°, are obtained, but no diphenyl*iso*chroman. Magnesium benzyl iodide gives with an excess of benzaldehyde amongst other products, dibenzoylphenylmethane and a small quantity of diphenyl*iso*chroman. The

formation of diphenyl*iso*chroman is held to be conditioned by the presence of excess of benzaldehyde. When heated with hydrochloric and acetic acids, diphenyl-*iso*chroman gives diphenylindene. From this and from the fact that a hydroxyl group was shown to be absent, the annexed formula is suggested for diphenyl*iso*chroman. From the formation of diphenyl*iso*chroman from benzaldehyde and magnesium benzyl bromide, the presence of a conjugated double bond in the latter compound is indicated. G. W. R.



Quinonemethides [Methylenequinones] and Pseudophenol-halogenides. II. H. LINDEMANN and H. FORTH (*Annalen*, 1923, **435**, 219—232).—An attempt has been made to prepare *o*-quinonemethides (cf. A., 1923, i, 686). 3 : 5-Dibromosalicyl-aldehyde is converted by thionyl chloride into a colourless *anhydro*-compound (m. p. 243°) (annexed formula). The tri- and mono-acetates of the aldehyde have m. p. 99—100° and 71°, respectively (Simonis and Wenzel, A., 1900, i, 496, give 103° and 90°, respectively). 3 : 5-Dibromo-2-methoxybenzaldehyde with phosphorus pentachloride gives the corresponding benzylidene *chloride* (needles, m. p. 76°), from which a quinonemethide cannot be obtained. 3 : 5-*Dibromo*-2-*hydroxybenzylidene chloride*, from phosphorus pentachloride and the corresponding aldehyde (in presence of benzene), forms needles, m. p. 97°. It is rapidly reconverted into the aldehyde when treated with warm alcohol or acetic acid, a cold solution in these solvents, when treated with water, becoming first orange (possibly owing to formation of quinonechloromethide) and then yellow (aldehyde). In the preparation of the last-named chloride, a *polymeride* of 3 : 5-dibromo-1 : 2-benzoquinone-1-chloromethide, m. p. 220—225°, is also formed.



3 : 5-Dibromosalicylaldehyde, with phosphorus pentabromide, gives, together with some anhydro-compound (m. p. 243°, above), the corresponding *bromide* (needles, m. p. 99°), the latter (or the corresponding chloride) giving an *acetyl* derivative (m. p. 113—114°) and an *anil*, red needles, m. p. 105°, and *imine*.

2-Hydroxy-4 : 6-dimethylbenzaldehyde, on bromination in presence of sodium acetate and acetic acid, affords the 3 : 5-*dibromo*-derivative, yellow needles, m. p. 190—191° (the *anil*, red needles, has m. p. 180—181°). The dibromo-aldehyde, which is unaffected by thionyl chloride, is converted by phosphorus pentachloride (in presence of phosphorus oxychloride) into the *anhydro*-derivative (m. p. above 300°) or (in presence of benzene) into the corresponding benzylidene *chloride* (needles, m. p. 114—115°), the latter, with aqueous alkali, giving first a transient orange colour (quinonemethide ?) and then the yellow colour of the aldehyde.

3 : 5-Dibromo-2-hydroxy-4-methoxybenzaldehyde (pale yellow needles, m. p. 97—98°; *triacetate*, m. p. 98°, *monoacetate*, m. p. 78°)

gives an *anil* (yellow needles, m. p. 105°) and an *imine* (m. p. 206°), the corresponding benzylidene *chloride* having m. p. 99°.

3 : 5-*Dibromo*-4-*hydroxy*-2-*methoxybenzaldehyde* has m. p. 170—171° (*triacetate*, m. p. 124°; *anil*, m. p. 185°), the corresponding benzylidene *bromide* having m. p. 111°. The latter, with aqueous alkali or ammonia gives successively a yellow, blue, and yellow colour, whilst, with sodium acetate solution, 3 : 5-*dibromo*-2-*methoxy*-1 : 4-*benzoquinone*-1-*bromomethide* is formed (yellow needles, m. p. 78—79°). The latter, when treated with water, gives the original aldehyde. The corresponding benzylidene *chloride* has m. p. 81° and affords the *chloromethide*, m. p. 98—100°.

2-Hydroxy-1-naphthaldehyde could not be converted into any derivatives of the type under discussion. E. E. T.

Compound of Cinnamaldehyde with Amylene. Nevenka Alujevich (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 292—294).—Exposure to the action of light in a glass tube of a mixture of cinnamaldehyde with excess of amylene results in the formation of an oily additive *compound*, $C_{14}H_{18}O$, which has the normal molecular weight in freezing benzene or acetic acid, but was not found capable of purification. The compound unites with bromine, yielding a brown *dibromide*, and gives benzoic acid when oxidised by means of permanganate. Reduction of the compound by means of hydriodic acid yields a small proportion of a product not yet identified, and treatment with phosphoric oxide gives a crystalline *compound*, m. p. 125°, also unidentified. T. H. P.

4 : 6-Dinitro*iso*phthalaldehyde. W. Borsche (*Ber.*, 1923, **56**, [*B*], 2357—2359).—It was shown previously (A., 1912, i, 180) that both methyl groups of 4 : 6-dinitro-*m*-xylene react with benzaldehyde to give 4 : 6-dinitro-1 : 3-distyrylbenzene. It is now found that the 4 : 6-dinitro-*m*-xylene does not react with nitrous acid to form the expected dialdoxime, but does react with *p*-nitrosodimethylaniline, in alcoholic solution in presence of sodium carbonate, to give 4 : 6-*dinitro*isophthalaldehyde-*bis*-p-*dimethylaminoanil*,

$$C_6H_2(CH{:}N{\cdot}C_6H_4{\cdot}NMe_2)_2(NO_2)_2,$$

a black, crystalline powder, m. p. 208°. This is readily hydrolysed by nitric acid in benzene suspension to 4 : 6-*dinitro*isophthalaldehyde, $C_6H_4(CHO)_2(NO_2)_2$, pale yellow needles, m. p. 132°. This gives a *dioxime*, bright yellow needles, m. p. 184°, and a *bisphenylhydrazone*, black needles, m. p. 251°. From benzene solution in sunlight, the aldehyde is gradually precipitated in the form of yellow needles, m. p. 185—186°, apparently of 4 : 6-*dinitroso*isophthalic *acid*. 4 : 6-Dinitro-*m*-xylene also reacts with mercuric chloride in presence of sodium ethoxide to form 4 : 6-*dinitro*isophthalylidenetetramercuri-*dioxide*, $C_8H_4O_6N_2Hg_4$, a heavy, yellow powder. E. H. R.

Electrolytic Oxidation of *iso*Eugenol. A. Lowry and C. M. Moore (*Trans. Amer. Electrochem. Soc.*, 1922, **42**, 273—284).—The authors have investigated a process for the production of vanillin by the electrolytic oxidation of *iso*eugenol, described in the German patent (D.R.-P. 92007). Experiments carried out with sodium

hydroxide or sulphuric acid as electrolyte gave in every case negative results. Vanillin itself is found to be readily oxidised electrolytically, and even if formed by the electrolytic oxidation it would be immediately converted into other products. Hence it is concluded that if vanillin is produced by the electrolytic oxidation, a totally different condition must prevail from that described in the patent. J. F. S.

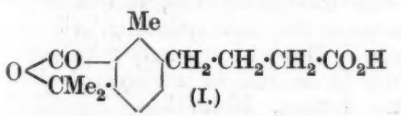
Acetyl Derivative of Deoxybenzoin (Tautomeric Form). C. V. Gheorgiu (*Ann. Scient. Univ. Jassy*, 1923, **11**, 307—308; from *Chem. Zentr.*, 1923, iii, 1159).—By treatment of deoxybenzoin with acetic acid and zinc chloride, a crystalline precipitate, m. p. 102—106°, held to be the *acetyl* derivative in the enol form,

$$CHPh{:}CPh{\cdot}OAc,$$

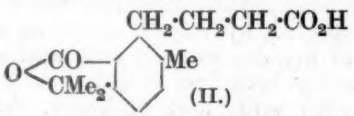
is obtained. On hydrolysis, however, it does not give the corresponding alcohol, but deoxybenzoin. G. W. R.

Electrolytic Reduction of Oximes. I. Benzoinoxime. Masayoshi Ishibashi (*Mem. Coll. Sci. Kyoto*, 1923, **7**, 39—44).—Benzoinoxime is only partly reduced electrolytically in acid solution. A part is hydrolysed before electrolytic reduction occurs, and the benzoin resulting from the hydrolysis is reduced to form hydrobenzoin, benzoinpinacone, and deoxybenzoinpinacone. Optimal conditions for the preparation of the amine require that the electrolysis be conducted at 19° to 20° with a current density of about 0·3 amp. per sq. cm., and that a cathode of tin or lead be employed. The concentration of sulphuric acid in the catholyte should not exceed 5%. In alkaline or neutral solution no appreciable electrolytic reduction or hydrolysis of benzoinoxime is observed. J. S. G. T.

Picrotin Ketone and Picrotinic Acid. F. Angelico and F. Monforte (*Gazzetta*, 1923, **53**, 800—807; cf. A., 1909, i, 318; 1910, i, 404, 576).—The failure of the action of sodium hypobromite on picrotin ketone to yield bromoform and that of the action of iodine and potassium hydroxide to give iodoform render doubtful Horrmann and Bischof's suggestion that the molecule of this ketone contains the grouping $\cdot CH_2 \cdot CO \cdot CH_3$ (A., 1922, i, 161). Fusion with potassium hydroxide of picrotinic acid, for which formula (I) or (II) may be assumed, yields, besides products of profound decomposition, a

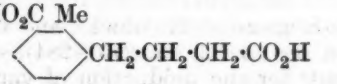


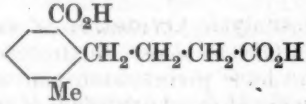
(I.)



(II.)

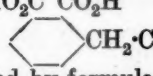
dicarboxylic acid, $C_{12}H_{14}O_4$, m. p. 132°, of constitution (III) or (IV). On the other hand, gradual oxidation of picrotinic acid yields a

(III.) 



(IV.)

series of acids of the formulæ $C_{15}H_{16}O_6$, $C_{13}H_{12}O_6$, and $C_{13}H_{12}O_7$, all

of which give acetone when fused with potassium hydroxide, and hence contain the phthalide grouping intact (A., 1910, i, 404). From its formula the acid $C_{15}H_{16}O_6$, known as picrotinphthaldicarboxylic acid, evidently contains a carboxyl group in place of the methyl group of picrotinic acid, so that its possible constitutions follow from formulæ (I) and (II). Since, when fused with potassium hydroxide, picrotinic acid loses only acetone and gives a dibasic acid, picrotinphthaldicarboxylic acid should, under similar conditions, yield a tribasic acid. A crystalline acid, m. p. about 153°, is indeed obtained in this way, but in quantity insufficient for analysis; since, however, it condenses with resorcinol in presence of sulphuric acid, to yield a fluorescent compound, it is probable that its formula is  , and that picrotinic acid is represented by formula (I).

Horrmann (A., 1916, i, 828) suggests that picrotin ketone and picrotinic acid may be derived from a β-ketonic acid,

$$CH_2R{\cdot}CO{\cdot}CH_2{\cdot}CO_2H,$$

which cannot be isolated, possibly owing to the readiness with which it loses carbon dioxide. Neither picrotin nor picrotoxinin has, however, yet yielded an oxime, and the authors find that the action of amyl nitrite on picrotin in presence of sodium ethoxide gives principally two nitrogen-free acids.

Oximinopicrotin ketone, $C_{14}H_{15}O_3N$, m. p. 215° (decomp.), is readily convertible into the *dioxime*, $C_{14}H_{14}O_4N_2$, which crystallises in minute needles, m. p. 232° (decomp.).

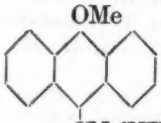
The *acid*, $C_{11}H_{14}O_5$ or $C_{13}H_{16}O_6$, obtained by treating picrotin with amyl nitrite and sodium ethoxide, forms minute crystals, m. p. 330°, and sublimes at the melting point, giving vapours which irritate the mucus. When heated with fused potassium hydroxide, it yields acetone, and with sulphuric acid and resorcinol it forms a fluorescein. It is accompanied by another *acid*, which contains C 54·29% and H 7·58%, and forms silky, white needles, m. p. 95°.

T. H. P.

Anomalous Splitting of Ketimides. F. KROLLPFEIFFER (*Ber.*, 1923, **56**, [*B*], 2360—2365).—The ketimides obtained by condensing anthranol methyl ether with nitriles are not, as was to be expected, hydrolysed by dilute acids to the corresponding ketones, but are decomposed into anthrone. Thus 10-methoxy-9-anthrylmethyl-ketimide decomposes with formation of methyl alcohol, acetic acid, and anthrone. The ketone, 10-methoxy-9-anthryl methyl ketone, is only obtained in small yield by boiling an aqueous solution of the hydrochloride of the ketimide; the ketone itself is readily hydrolysed to anthrone. The phenyl derivative, 10-methoxy-9-anthryl-phenyl-ketimide, is much more stable than the methyl compound; it is only hydrolysed by boiling concentrated hydrochloric acid, giving anthrone and benzoic acid. The *N*-methyl derivative of this ketimide is likewise hydrolysed by boiling concentrated hydrochloric acid, forming anthrone, methylamine, and

benzoic acid. The readiness with which the acyl residue is removed in the anthryl ketones appears to be influenced by the μ-methoxy group, for μ-anthryl phenyl ketone is not hydrolysed by hot hydrochloric acid in acetic acid solution, although with warm concentrated sulphuric acid it gives anthracenesulphonic acid and benzoic acid.

10-*Methoxy*-9-*anthryl-methyl-ketimide* (annexed formula) is obtained by mixing anthranol methyl ether and acetonitrile with aluminium chloride and passing a current of dry hydrochloric acid through the cooled mixture; it forms a pale yellow, crystalline powder, m. p. 145—146°. 10-*Methoxy*-9-*anthryl methyl ketone* forms pale yellow, glistening, square leaflets, m. p. 182—183°. 10-*Methoxy*-9-*anthryl-phenyl-ketimide* forms stout, yellowish-green crystals, m. p. 147—148°; its *hydrochloride* forms an orange, crystalline precipitate. 10-*Methoxy*-9-*anthryl-phenyl*-N-*methyl-ketimide* is obtained by methylating the ketimide with methyl sulphate; it forms pale yellow needles, m. p. 127°. E. H. R.



2 : 3-Diaminoanthraquinone. Society for Chemical Industry in Basle (Swiss Pat. 98312; from *Chem. Zentr.*, 1923, iv, 829).—3-Bromo-2-aminoanthraquinone is treated with aqueous or ethyl-alcoholic ammonia in the presence or absence of catalysts at 170—190° under pressure. 2 : 3-*Diaminoanthraquinone* thus obtained is crystalline. G. W. R.

Derivatives of β-Methylanthraquinone. III. The Synthesis of *Frangula* Emodin. R. Eder and C. Widmer (*Helv. Chim. Acta*, 1923, **6**, 966—981).—It is known that emodin is a trihydroxy-β-methylanthraquinone, and it is highly probable that two of the hydroxyl groups are in the 1 : 8-positions and the methyl group in the 3-position as in chrysophanic acid. It is also probable that the third hydroxyl is in a β-position and not adjacent to an α-hydroxyl group. These probabilities have now been confirmed by synthesis and the constitution of emodin established as 1 : 6 : 8-trihydroxy-3-methylanthraquinone. The synthesis was accomplished in a manner similar to that of chrysophanic acid (A., 1923, i, 688), starting from 3 : 5-dinitrophthalic acid and *m*-cresol. 3 : 5-*Dinitrophthalic anhydride* is formed by boiling the acid with acetic anhydride; it crystallises in white, stout, hygroscopic needles, m. p. 163—164°. It condenses with *m*-cresol in presence of aluminium chloride to give 3 : 5-*dinitro*-o-3′-*hydroxy*-p-*toluoylbenzoic acid*, greenish-yellow leaflets, m p. 236—237°. This compound is very sensitive to alkalis, forming a *compound*, $C_{15}H_{11}O_6N$, white needles, m. p. 251—252° (decomp.). It corresponds in composition with a nitrohydroxytoluoylbenzoic acid, but could not be identified as such a compound. It can be reduced to an *amino*-compound, yellow needles, m. p. 305—306° (decomp.). 3 : 5-Dinitro-*o*-3′-hydroxy-*p*-toluoylbenzoic acid is reduced by ferrous sulphate and ammonia to 3 : 5-*diamino*-o-3′-*hydroxy*-p-*toluoylbenzoic acid*, pale

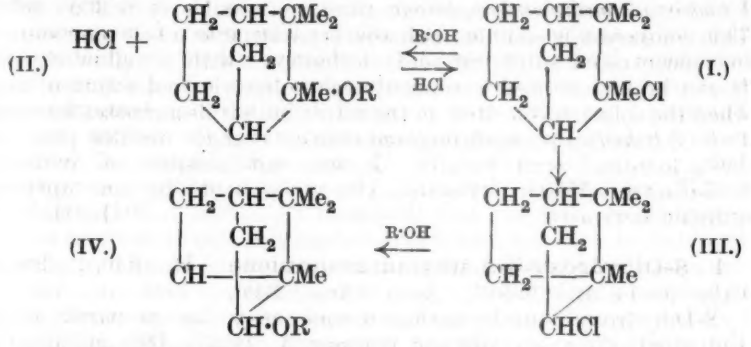
yellow needles, m. p. 233—234°. When heated in concentrated sulphuric acid at 160—170°, this is converted into 6 : 8-*diamino*-1-*hydroxy*-3-*methylanthraquinone*, stout, red needles, m. p. 306—307°. This compound is soluble in alkalis, separating as a salt on cooling; in concentrated sulphuric acid, it dissolves with a yellow colour. It can be tetrazotised in concentrated sulphuric acid solution, and when the solution is heated on the water-bath it decomposes forming 1 : 6 : 8-*trihydroxy*-3-*methylanthraquinone*, orange needles, m. p. 256°, identical with emodin. It was not possible to condense 3 : 5-dinitro-*o*-3′-hydroxy-*p*-toluoylbenzoic acid to an anthraquinone derivative. E. H. R.

1 : 8-Dihydroxy-3-methylanthraquinone. R. EDER (Swiss Pats. 95614 and 95947; from *Chem. Zentr.*, 1923, iv, 664).—1 : 8-Dihydroxy-3-methylanthraquinone may be prepared from α-nitrophthalic acid (Eder and Widmer, A., 1922, i, 260) and also by condensation of α-aminoacetylphthalic acid with *m*-cresol in the presence of aluminium chloride to 3-amino-*o*-2′-hydroxy-*p*-toluoylbenzoic acid, from which 1 : 8-dihydroxy-3-methylanthraquinone is obtained by way of the diazo-compound, or by heating with strong sulphuric acid at 150°, whereby 8-*amino*-1-*hydroxy*-3-*methylanthraquinone*, reddish-brown needles, m. p. 237—238°, is obtained. The latter, by diazotisation and boiling, yields the 1 : 8-dihydroxy-compound. G. W. R.

Intramolecular Displacements of Atoms. I. Addition of Alcohols to Camphene. H. MEERWEIN and L. GÉRARD (*Annalen*, 1923, **435**, 174—189).—Semmler (A., 1901, i, 90), by treating camphene with alcohols in presence of sulphuric acid, obtained, as he supposed, *iso*bornyl ethers, which are similarly obtainable from *iso*borneol. A precise proof of the constitution of the ethers is now given for the first time. *iso*Bornyl methyl ether is formed by the interaction of camphene, methyl alcohol, and sulphuric acid, or by that of methyl iodide and sodium bornyloxide, and is quite distinct from the methyl ether of camphene hydrate, obtained from the potassium derivative of camphene hydrate and methyl iodide.

The results recorded previously (A., 1920, i, 855) in connexion with the action of alcohols on camphene hydrochloride have an interesting sequel. If a solution of camphene hydrochloride in an alcohol is kept at 20°, the concentration of free hydrogen chloride (cf. A., 1922, ii, 751), initially high, slowly falls to a minimum (after several days) and then slowly rises to 100% of that present originally. These phenomena are due to the following processes: (1) Reversible interaction of camphene hydrochloride (I) and alcohol to give hydrogen chloride and an ether (II). This interconversion is entirely analogous to that of triphenylchloromethane and triphenylcarbinyl ethers (a little of II decomposes into camphene and alcohol). (2) Isomerisation of unchanged camphene hydrochloride into *iso*bornyl chloride (III). As a result of this, the change II ⟶ I is promoted, until no more ether remains.

(3) Interaction of *iso*bornyl chloride with alcohol to give *iso*bornyl ethers (IV):



This scheme was suggested by the results of a determination (against time) of the relative proportions of free hydrogen chloride, *iso*bornyl chloride, and camphene hydrochloride in such a system, starting with camphene hydrochloride and an alcohol. With methyl alcohol, a maximum content of *iso*bornyl chloride is present at the time corresponding with the above minimum concentration of hydrogen chloride. Proof of the explanation given is afforded in the following:

If an ethereal solution of camphene hydrochloride is slowly added to a methyl-alcoholic suspension of anhydrous potassium carbonate, so that the solution never becomes acidic, camphene hydrate methyl ether is obtained (in 50% yield), identical with the product from the action of methyl iodide on the potassium derivative of camphene hydrate (this preparation being effected in xylene suspension, unchanged camphene being finally removed by means of ozone). *Camphene hydrate methyl ether* has m. p. 12—14°, b. p. 201·5°, or 88·5—89°/17 mm., d_4^{20} 0·9477—0·9481, and n_D^{20} 1·47153 (mean constants of the two samples obtained). Active camphene, $[\alpha]_D^{21}$ +50·75° when converted, through the hydrochloride into the ether, gives the latter with $[\alpha]_D^{21}$ −12·71°. When shaken with a solution containing potassium ferrocyanide and hydrochloric acid, the methyl ether affords an *additive* compound, $3C_{10}H_{17}OMe,H_4Fe(CN)_6$.

Whilst *camphene hydrate ethyl ether* could not be obtained from camphene hydrate, it is readily obtained (although in small yield, because of its sensitivity to acids) from camphene hydrochloride, potassium carbonate, and ethyl alcohol, and forms a colourless oil (b. p. 93°/17 mm., d_4^{20} 0·9350), decomposing at 200° into camphene and alcohol.

If camphene hydrochloride is allowed to remain in methyl-alcoholic solution for about fourteen days at 30°, or until the concentration of free hydrogen chloride no longer increases, *iso*bornyl methyl ether results; if the above active camphene is used, the resulting ether has $[\alpha]_D^{25}$ −23·4°. Semmler's method, using active camphene, gives the ether with $[\alpha]_D^{21}$ −14·82°, a rotation decreased

by prolonging the action of the methyl-alcoholic sulphuric acid. (This preparation depends on the initial formation of camphene hydrate sulphuric ester, which changes into the *iso*bornyl ester, this with alcohol giving the ether. The rate of conversion of camphene hydrate esters into *iso*bornyl ethers is greater with sulphuric and aromatic sulphonic esters than with halogen esters.) Similarly, the ether was obtained from sodium bornoxide and methyl iodide, the mean physical constants of the various products being: b. p. 191—191·5°, 78°/17 mm. or 80°/19 mm., d_4^{20} 0·9250—0·9277, n_D^{20} 1·46252—1·46282. The unstable additive compounds described by Bertram and Walbaum (A., 1894, i, 204) could not be obtained. It was found that *iso*bornyl methyl ether was readily converted by hydrogen bromide into *iso*bornyl bromide, hydrogen chloride acting similarly, but more slowly.

When treated with hydrochloric acid and potassium ferrocyanide, the ether gives an *additive* compound, $3C_{10}H_{17}OMe,H_4Fe(CN)_6$, decomposing at 170°, whilst on heating with anhydrous zinc chloride it gives camphene and methyl alcohol, stannic chloride effecting the same change more slowly, whilst other metallic chlorides are without action.

*iso*Bornyl methyl ether is also formed by warming camphene hydrate methyl ether with methyl-alcoholic hydrogen chloride, or by treating *iso*bornyl chloride with methyl alcohol. Camphene hydrate methyl ether is rapidly decomposed, whereas *iso*bornyl methyl ether is unaffected, by glacial acetic acid at 80°. The camphene produced (through the first-formed camphene hydrate acetate) is readily estimated by titration with perbenzoic acid so that mixtures of the two ethers may readily be analysed.

Camphene hydrate ethyl ether affords camphene even when shaken for a few hours with 1% sulphuric acid, the methyl ether being practically unaffected by the latter. The methyl ether is rapidly converted by traces of zinc, stannic, aluminium, ferric, and mercuric chlorides or antimony pentachloride into camphene and methyl alcohol (cf. *iso*bornyl methyl ether), whilst hydrogen chloride and bromide decompose both hydrate ethers to give camphene hydrochloride (hydrobromide), this passing rapidly into *iso*bornyl chloride (bromide). E. E. T.

[Intramolecular Displacements of Atoms.] II. Camphor dichloride. [2 : 2-Dichlorocamphane]. H. MEERWEIN and R. WORTMANN (*Annalen*, 1923, **435**, 190—206).—The conversion: $CMe_3\cdot CHMe\cdot OAcyl \rightleftarrows CMe_2(OAcyl)\cdot CHMe_2$ may be regarded as a result of ionisation, followed by intra-ionic rearrangement, $(CMe_3\cdot CHMe)\overset{+}{O}\cdot\overset{-}{Acyl} \rightleftarrows (CMe_2\cdot CHMe_2)\overset{+}{O}\cdot\overset{-}{Acyl}$, free radicals not being involved. The ordinary pinacone–pinacolin change may, similarly, be written:

$$(CMe_2\cdot CMe_2\cdot OAcyl)\overset{+}{O}\cdot\overset{-}{Acyl} \longrightarrow (CMe_3\cdot CMe\cdot OAcyl)\overset{+}{O}\cdot\overset{-}{Acyl},$$

the reverse change not occurring, owing to the instability of pinacolin esters other than those with halogen acids. Pinacolin dichloride [γγ-dichloro-ββ-dimethylbutane] and pinacone dichloride

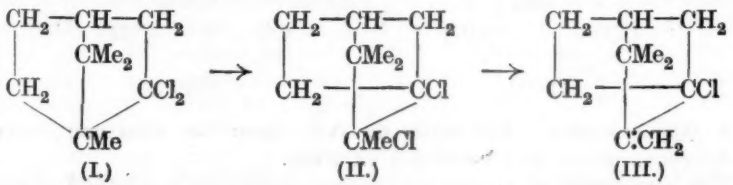
[βγ-dichloro-βγ-dimethylbutane] cannot be interconverted, but if the vapours of the first substance be passed over barium chloride, heated at 400—450°, a little βγ-dimethylbutadiene results, probably owing to the intermediate formation of pinacone dichloride.

Greater powers of isomerisation would be expected from 2 : 2-dichlorocamphane, which possesses a similar structure to pinacolin dichloride. The substance described as dichlorocamphane by previous authors (*e.g.*, Bredt, A., 1901, i, 217; Marsh and Gardner, T., 1897, **71**, 290; Marsh and Hartridge, T., 1898, **73**, 852) is now shown to be a mixture of substances. If, however, a mixture of camphor (200 g.), phosphorus trichloride (170 g.), and pure phosphorus pentachloride (294 g.) is left at 0° for a month, pure *α-camphor dichloride* (2 : 2-*dichlorocamphane*) (I) is obtained, m. p. 146—148° (decomp.). Occasional preparations fail, and it is always necessary to test the product by studying its interaction with sodium ethoxide (boiling alcoholic solution) or with methyl alcohol (at 50°), which proceeds in a characteristic manner.

When heated with a mixture of phenol and potassium acetate, 2 : 2-dichlorocamphane affords *α-chlorocamphene* (III) (colourless, setting point about 20°, b. p. 193—197°), this, on reduction with sodium and alcohol affording camphene (setting point 44·5°, b. p. 156·5—158°), and on ozonolysis giving *α-chlorocamphenilone*. The latter compound (in which CO replaces the hemi-cyclic CH_2 group in III) has setting point, 14·5°, b. p. 116—118°/18 mm., gives a *semicarbazone*, m. p. 206—207° (mixed with a little *β-chlorocamphenilone semicarbazone*?) and an *oxime*, m. p. 210—211°.

Pinacolin dichloride with phenol and potassium acetate gives *β-chloro-γγ-dimethyl-Δ$^{\alpha}$-butene*, no intramolecular change occurring.

The conversion of 2 : 2-dichlorocamphene into α-chlorocamphene occurs according to the scheme:



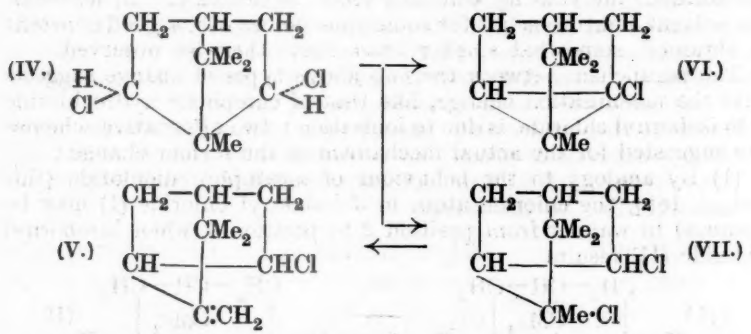
(I.) (II.) (III.)

the intermediate *α-chlorocamphene hydrochloride* (II) being obtainable by combining α-chlorocamphene and hydrogen chloride. This hydrochloride is less easily decomposed than camphene hydrochloride, but is completely decomposed by methyl alcohol at 50° in half an hour. This shows that the dichlorocamphane of previous authors contained, at most, traces of α-chlorocamphene hydrochloride.

The isomerism between pinacolin dichloride and pinacone dichloride is now seen to be similar to that between dichlorocamphane and α-chlorocamphene hydrochloride: $CMe_3·CMeCl_2 \rightarrow CMe_2Cl·CMe_2Cl$, so that the present work affords a first confirmation of the authors' views with regard to the pinacolin change (above). Moreover, 2 : 2-dichlorocamphane may undergo the retrograde

change. If, in its preparation, the temperature is allowed to rise, or if impure phosphorus pentachloride is used, an isomeride, β-*camphor dichloride* (colourless crystals, m. p. 178—179°), is the main product. This substance is easily distinguished from its α-isomeride by its much smaller rate of reaction with 0·2*N* sodium ethoxide (or methyl alcohol), and is best prepared by treating α-camphor dichloride, in toluene solution, with stannic chloride until the product no longer reacts rapidly with sodium ethoxide (or methyl alcohol).

On reduction, β-camphor dichloride affords camphane, and, on warming with phenol and potassium acetate, gives a mixture of β-*chlorocamphene* (V) and *chlorotricyclene* (VI), as was proved by the fact that this mixture, on reduction with sodium and alcohol, afforded tricyclene and camphene. The latter, but not tricyclene, is oxidised by ozone, and the mixture can thus be identified. Again, the mixture of β-chlorocamphene and chlorotricyclene, on treating with ozone, gave a mixture of chlorotricyclene (m. p. 134—135°, b. p. 194—196°) and β-*chlorocamphenilone*, needles, m. p. 162—163° (semicarbazone, m. p. 244—245°). β-Camphor dichloride is therefore *trans*-2 : 6-dichlorocamphane (IV), the above reactions being expressed :



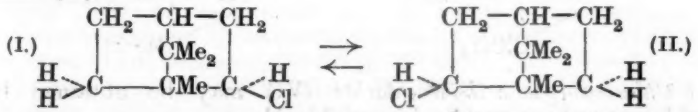
β-*Chlorocamphene hydrochloride* (VI) may be obtained from β-chlorocamphene and hydrogen chloride.

The conversion of α- into β-camphor dichloride is effected under conditions causing the change of camphene hydrochloride into *iso*bornyl chloride. The conversion is rapid in phenol solution, but very slow in most solvents, unless stannic chloride or antimony pentachloride is present. The dielectric constant of the solvent is of far greater influence than the nature of the catalyst, the change being very slow in light petroleum, more rapid in benzene, and still more rapid in the ionising solvents, chlorobenzene and nitrobenzene. The case is evidently one of the intra-ionic isomerisation of esters, no tricyclene compounds being necessarily involved. Into the same class of change may be put the relationships (hitherto unexplained) between fenchyl alcohol, α-fenchene hydrate, *iso*fenchyl alcohol, and β-fenchene hydrate (these relationships being shown schematically in the paper). E. E. T.

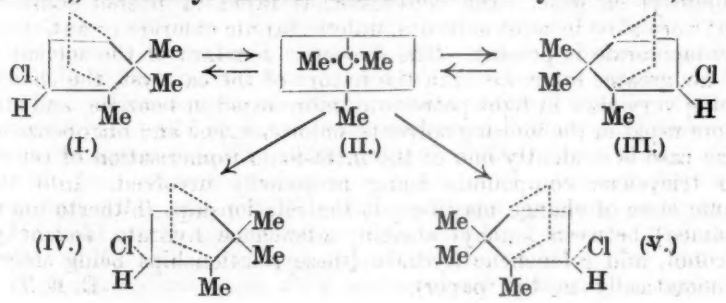
[**Intramolecular Displacements of Atoms.**] **III. Racemisation Phenomena in the Camphor Series.** H. MEERWEIN and F. MONTFORT (*Annalen*, 1923, **435**, 207—218).—Optically active *iso*bornyl esters undergo racemisation under conditions specially favouring the rapid conversion of camphene hydrate esters into *iso*bornyl esters (A., 1922, ii, 751). *iso*Bornyl chloride undergoes complete racemisation in three hours in cresol solution at 20°. In most solvents, racemisation is too slow to follow, and the use of catalysts is to be avoided, owing to their tendency to form additive compounds with the solvent, with resulting decay of activity. To overcome this difficulty, the velocity of racemisation has been measured in cresol, and in mixtures of this solvent with nitromethane, nitrobenzene, bromobenzene, chlorobenzene, ethyl bromide, benzene, light petroleum, benzonitrile, anisole, acetonitrile, and ether. It is found that, except in the cases of acetonitrile, benzonitrile, and anisole, which form additive compounds with cresol, the order of solvents from the point of view of decreasing racemisation velocities is the same as that of the velocity of conversion of camphene hydrochloride into *iso*bornyl chloride (*loc. cit.*), which in turn is (approximately) the order of decreasing dielectric constants. In the three cases where additive compounds are formed, the velocity constant tends to decrease. If, however, the solvent-mixture is left for some time before use, a good constant is obtained, somewhat smaller than that otherwise observed.

The parallelism between the two above types of change suggests that the racemisation change, like that of camphene hydrochloride into *iso*bornyl chloride, is due to ionisation; two alternative schemes are suggested for the actual mechanism of the former change:

(1) By analogy to the behaviour of α-camphor dichloride (this vol., i, 188), the chlorine atom in *d-iso*bornyl chloride (I) may be assumed to wander from position 2 to position 6, when *l-iso*bornyl chloride (II) results:



(2) The second suggested scheme is self-explanatory (I to V being, respectively, *d-iso*bornyl chloride, the *iso*bornyl-ion (plane formula), *l-iso*bornyl chloride and *d*- and *l*-bornyl chlorides):



This would account for the observed formation of bornyl chloride during the racemisation of *iso*bornyl chloride (*loc. cit.*). E. E. T.

The Rotation-dispersion of some Homologous Methylenecamphor Derivatives. H. RUPE and C. COURVOISIER (*Helv. Chim. Acta*, 1923, **6**, 1049—1071).—The method described by Rupe and Burckhardt for the synthesis of β-camphorylidenepropionic acid from chloromethylenecamphor and ethyl sodioacetoacetate (A., 1917, i, 141) is a general one, and has now been used for the synthesis of a number of homologous acids, from chloromethylenecamphor and ethyl alkylacetoacetates. Since the acids readily lose carbon dioxide when heated, giving alkylmethylenecamphors, a general method is provided for the synthesis of these compounds. It was found that the optical rotations of these alkylidenecamphors changed when the substances were repeatedly distilled. This phenomenon is to be attributed to *cis-trans*-isomerism, and in the case of ethylmethylenecamphor it is probable that at least one isomeride was obtained in the pure form. This isomeric change during distillation accounts for the different values for the optical rotation of methylmethylenecamphor recorded by different observers. The rotations of the compounds described were measured for four different wave-lengths, and all showed normal rotation-dispersion.

Ethyl β-*camphorylidene*-α-*methylpropionate*,

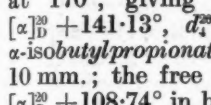
$$C_8H_{14}<\begin{matrix}CO\\ C:CH\cdot CHMe\cdot CO_2Et'\end{matrix}$$

obtained from chloromethylenecamphor and ethyl methylacetoacetate by the action of sodium ethoxide, distils at 164—167°/12 mm. It is hydrolysed by boiling in a mixture of glacial acetic acid and fuming hydrochloric acid. The free β-*camphorylidene*-α-*methylpropionic acid* is purified through its calcium salt and by distillation. It forms an oil which crystallises slowly in bunches of needles, m. p. 109—110°. It decomposes at 160°, giving a quantitative yield of *ethylmethylenecamphor* (n-*propylidenecamphor*), b. p. 113—116°, $[\alpha]_D^{20}$ +149·81°, d_4^{20} 0·9497 (prepared from non-crystalline acid), or $[\alpha]_D^{20}$ +73·26°, d_4^{20} 0·9533 (from the crystalline acid). The latter product partly crystallised in white needles, m. p. 41—43°, giving in benzene $[\alpha]_D^{20}$ +22·67°, $[\alpha]_F/[\alpha]_C$ 2·16°. The crystalline product is probably a pure isomeride, but whether *cis* or *trans* it is impossible to say. *Ethyl* β-*camphorylidene*-α-*ethylpropionate*, from ethyl ethylacetoacetate and chloromethylenecamphor, is a pale yellow, bitter liquid, b. p. 169°/12 mm. The free *acid* forms silky, white needles, m. p. 118°; the *calcium* salt forms bunches of short, white needles. The free acid begins to decompose at 125°, giving a quantitative yield of n-*butylidenecamphor*, b. p. 130—131°/12 mm., $[\alpha]_D^{20}$ +94·58°, d_4^{20} 0·9389, $[\alpha]_F/[\alpha]_C$ 2·36. *Ethyl* β-*camphorylidene*-α-*propylpropionate*, from ethyl *n*-propylacetoacetate and chloromethylene camphor, has b. p. 176—179°/9·5 mm.; the free *acid* has m. p. 95—96°. n-*Valerylidenecamphor* has b. p. 139—141°/12 mm., $[\alpha]_D^{20}$ +116·48°, d_4^{20} 0·9332, $[\alpha]_F/[\alpha]_C$ 2·36. The condensation of ethyl sodio*iso*propylacetoacetate with chloromethylenecamphor

was unsatisfactory, but ethyl sodiobutylacetoacetate condensed normally, forming *ethyl* β-*camphorylidene*-α-n-*butylpropionate*, a yellow oil, b. p. 191—193°/11 mm.; the free *acid* can be crystallised with difficulty in white needles, m. p. 76°. The acid decomposes at 170°, giving n-*hexylidenecamphor*, b. p. 147—149°/13 mm., $[\alpha]_D^{20}$ +141·13°, d_4^{20} 0·9252, $[\alpha]_F/[\alpha]_C$ 2·37. *Ethyl* β-*camphorylidene*-α-iso*butylpropionate* is a viscous, pale yellow oil, b. p. 183—185°/10 mm.; the free *acid* forms white needles, m. p. 97—98°; it has $[\alpha]_D^{20}$ +108·74° in benzene. iso*Amylmethylenecamphor*,

$$C_8H_{14}<\begin{matrix}CO\\ |\\ C{:}CH\cdot[CH_2]_2\cdot CHMe'\end{matrix}$$

is a viscous oil, b. p. 144—146°/12 mm., $[\alpha]_D^{20}$ +133·84°, d_4^{20} 0·9202, $[\alpha]_F/[\alpha]_C$ 2·35. β-*Camphorylidene*-α-*allylpropionic acid* (annexed formula) has m. p. 95°; its *ethyl* ester is a mobile oil, b. p. 183—185°/11 mm. The acid loses carbon dioxide normally when heated, giving α-*camphorylidene*-Δ^{δ}-*pentene*, a pale yellow, mobile oil having an odour of camphor and garlic, b. p. 136—137°/11 mm., $[\alpha]_D^{20}$ +144·23°, d_4^{20} 0·9475, $[\alpha]_F/[\alpha]_C$ 2·37. β-*Camphorylidene*-α-*benzylpropionic acid* forms white, silky crystals, m. p. 127°; the *ethyl* ester is a pale yellow, viscous oil, b. p. 226—228°/12 mm.; the *sodium* salt is very sparingly soluble. Distillation of the acid gives *phenylpropylidenecamphor*, a pale yellow, viscous oil, b. p. 204—206°, $[\alpha]_D^{20}$ +126·92°, d_4^{20} 1·0104, $[\alpha]_F/[\alpha]_C$ 2·36. *Camphorylidenemethylsuccinic acid*, $C_8H_{14}<\begin{matrix}CO\\ |\\ C{:}CH\cdot CH\cdot CO_2H\end{matrix}\begin{matrix}CH_2\cdot CO_2H\\ |\\ \end{matrix}$, crystallises in bunches of small, white needles, m. p. 158°; the *ethyl* ester is a yellow, viscous oil, b. p. 219—222°/12 mm. Distillation of the dicarboxylic acid at 190—215°/12 mm. gives γ-*camphorylidenebutyric acid*, a viscous, yellow oil, b. p. 210—213°/10 mm., $[\alpha]_D^{20}$ +32·31°, in benzene, d_4^{20} 0·9078.



In the course of the work, a number of by-products were obtained. In several cases, the *cis*-form of dicamphoethandiene (A., 1919, i, 335) was isolated from the reaction product. Another class of by-product resulted from the fact that the β-camphorylidenepropionic acid and its derivatives form sodium derivatives which can react with a second molecule of chloromethylenecamphor, forming dicamphorylidene derivatives. The following compounds of this type were identified. *Ethyl di*(*camphorylidenemethyl*)-*propionate*, $\left(C_8H_{14}<\begin{matrix}CO\\ |\\ C{:}CH\end{matrix}\right)_2{:}CMe\cdot CO_2Et$, m. p. 118°; *ethyl di*(*camphorylidenemethyl*)-n-*butyrate*, m. p. 161°; *ethyl di*(*camphorylidenemethyl*)-n-*valerate*, m. p. 175°; *ethyl di*(*camphorylidenemethyl*)*allylacetate*, m. p. 148°, and *ethyl di*(*camphorylidenemethyl*)*succinate*, m. p. 105°.

E. H. R.

Action of Ferric Chloride on Hydroxymethylenecamphor. H. Rupe and M. Schärer (*Helv. Chim. Acta*, 1923, **6**, 1072—1076).—When hydroxymethylenecamphor is boiled for some hours in alcoholic solution with ferric chloride, α-chlorocamphor is formed;

in the same manner, ferric bromide gives α-bromocamphor. To explain the reaction, it may be assumed that hydrochloric acid combines with the hydroxymethylenecamphor, forming hydroxymethylchlorocamphor, which reacts with water, forming chlorocamphor and formic acid. Prolonged action of ferric chloride on hydroxymethylenecamphor results in the formation of camphoric anhydride, probably with camphorquinone as an intermediate stage. E. H. R.

Preparation of Menthyl Diethylaminoethylcarbamate. Society for Chemical Industry in Basle (Swiss Pat. 99625; from *Chem. Zentr.*, 1923, iv, 829).—Menthyl halogen formates are treated with at least the molecular quantity of diethylethylenediamine, $NH_2 \cdot CH_2 \cdot CH_2 \cdot NEt_2$. *Menthyl diethylaminoethylcarbamate*, thus prepared from an ethereal solution of menthyl chloroformate and an aqueous solution of diethylethylenediamine, with agitation and cooling, is an oil having b. p. 142°/0·015 mm. G. W. R.

The Action of Phenylhydrazine on Pinene Nitrosochloride. R. E. Kremers (*J. Amer. Pharm. Assoc.*, 1922, **11**, 604—606).—Phenylhydrazine and pinene nitrosochloride, when allowed to react in 95% ethyl alcohol, yielded phenylhydrazine hydrochloride, an unidentified *substance*, yellow crystals, m. p. 147—148°, and a *substance*, $C_{16}H_{21}N_2$, faintly yellow, hard prisms, m. p. 148—150°. Chemical Abstracts.

Stick-lac. A. Tschirch and F. Lüdy, jun. (*Helv. Chim. Acta*, 1923, **6**, 994—1008; cf. Tschirch and Farner, A., 1899, i, 446).—A systematic investigation has been made of Indian stick-lac, the resin formed by a species of louse, *Tachardia lacca*, parasitic on certain trees in the East. The aqueous extract contains one of the dyes present in the stick-lac; this is precipitated by lead acetate as a violet lake. The filtrate contains dextrose and lævulose, besides albumin; the ash from the evaporated filtrate contains nitrogen, sulphur, potassium, and calcium. The lac appears to contain invert-sugar, probably formed enzymatically by the insect from the sucrose of the tree. The red dye, laccaic acid, is obtained from the lead acetate precipitate by extraction with alcohol containing hydrochloric acid; it crystallises in stout, red prisms. Dimroth and Goldschmidt (A., 1913, i, 981) failed to prove that the dye is an anthraquinone derivative; this has now been done by distillation with zinc dust. In dilute alcohol, laccaic acid shows absorption bands at λ 0·545—0·520 μ and 0·510—0·488 μ. Since the dye is formed in the *Tachardia* by a yeast-like organism, it is interesting to find that its absorption bands are very similar to those shown by the colouring matters from red yeasts and bacteria. In concentrated sulphuric acid, laccaic acid dissolves with a carmine-red colour, showing the bands λ 0·590—0·560 μ, 0·540—0·520 μ, and 0·505—0·490 μ, and in sodium hydroxide solution its colour is reddish-violet with the three bands λ 0·610—0·575 μ, 0·555—0·533 μ, and 0·510—0·490 μ. The dye is a good indicator, the change from yellow (acid) to violet (alkali) being sharp. Alkaline solutions of the dye are unstable. Dyeings on silk and wool from an acid bath

are very fast to light. The constitution of the dye is as yet unknown. Although it is probably a glucoside, no sugar could be obtained from it by hydrolysis. Extraction of the residue from the aqueous extraction of the stick-lac with cold alcohol removes the resin, the perfume, and a second dye, erythrolaccin. The alcoholic extract is poured into dilute hydrochloric acid and the precipitate filtered off, dried, and extracted with ether. The ethereal extract is evaporated, and from the residual resinous oil the erythrolaccin crystallises in yellow leaflets. The crystals can be freed from resin by means of chloroform. The dye can be sublimed, forming red, felted crystals. Its yellow solution in an ether–alcohol mixture has a band at λ 0·510—0·485 μ; with sodium hydroxide, there are two bands, at λ 0·615—0·590 μ and 0·572—0·548 μ. The bluish-violet solution in concentrated sulphuric acid shows four bands at λ 0·680—0·640 μ, 0·610—0·590 μ, 0·560—0·540 μ, and 0·525—0·500 μ. It forms a *tetra-acetyl* derivative, green, oblique tablets, and is probably a *tetrahydroxymethylanthraquinone*. From an alkaline solution of the resins, after separation of the erythrolaccin, ether extracts the perfume, which crystallises in tablets having the characteristic shellac odour. The portion of the resins soluble in ether contains, besides aleuritic acid, shown by Harries and Nagel to be a trihydroxypalmitic acid (A., 1922, i, 522), a *monohydroxypalmitic acid*, m. p. 76·5—77°, and probably other fatty acids. These are probably present as lactides. The resin insoluble in ether is soluble in hot alcohol, and can also be hydrolysed, giving aleuritic acid. *Ethyl aleurate* crystallises in long needles, m. p. 57—58°. The residue from the stick-lac, when extracted with boiling alcohol, gives a wax crystallising in colourless leaflets, m. p. 82°, from which, by hydrolysis, an alcohol, *tachardiacerol*, $C_{24}H_{50}O$, m. p. 81—82°, and an *acid*, m. p. 74—76°, were obtained. The remainder of the wax was extracted by boiling benzene; this fraction has been examined by Gascard (A., 1914, i, 1045). After these extractions, the residue of the stick-lac consists only of the skeleton of the *Tachardia* with a little adsorbed laccaic acid.

E. H. R.

Scission of Potassium Atractylate. F. Angelico and F. Monforte (*Gazzetta*, 1923, **53**, 808—812; cf. A., 1907, ii, 122; 1910, i, 403).—Potassium atractylate, the glucoside of *Atractylis gummifera*, or either of its decomposition products, atractyliretin and atractyligenin, serves as an excellent colour reagent for aromatic hydroxy-aldehydes in general. The reagent is treated first with a little concentrated sulphuric acid and, after a few minutes, with a drop of an aqueous solution of the hydroxy-aldehyde; a red coloration similar to that of rosolic acid is obtained, the exact tint varying somewhat with the aldehyde employed.

Estimation of the sulphur and potassium present in, and of the valeric acid and dextrose formed on hydrolysis of, a sample of potassium atractylate gives results in agreement with the formula $C_{30}H_{52}O_{18}S_2K_2$. Atractyligenin, $C_{14}H_{22}O_4$, obtained by hydrolysing the glucoside and afterwards acidifying the liquid, forms

white crystals, m. p. 168°, and does not reduce Fehling's solution. Atractyliretin, prepared by prolonged boiling of the glucoside with normal sulphuric acid, is obtained as a white compound which hardens when it is triturated with water and then forms a white powder, m. p. about 190° (decomp.); like the isomeric atractyligenin, it exhibits acid properties and does not react with hydroxylamine or phenylhydrazine. T. H. P.

Loganin or Meliatin? M. BRIDEL (*Bull. Soc. Chim. biol.*, 1923, **5**, 801—805).—The work of Rosenthaler recently has shown that the glucoside loganin, originally described by Dunstan and Short (A., 1885, 395), is a mixture of meliatin (A., 1910, i, 692) and another substance not identified. The name loganin has therefore no longer any significance. C. R. H.

The Saponins of the Sarsaparilla Root. H. P. KAUFMANN and C. FUCHS (*Ber.*, 1923, **56**, [*B*], 2527—2533).—An investigation of the saponins of sarsaparilla root imported from Honduras in 1918; the date of harvesting is uncertain.

The ash contains the following substances expressed as percentages of the dried root: SiO_2, 1·25; Al_2O_3, 0·79; CaO, 0·57; MgO, 0·50; K_2O, 1·51; Cl, 0·46.

The finely divided root is extracted successively with chloroform, light petroleum, benzene, ether, anhydrous alcohol, and aqueous alcohol (50%). The light petroleum extract contains cetyl alcohol. The saponins are isolated as a form soluble in absolute alcohol (saponin *A*) and an insoluble form (saponin *B*). Saponin *A* is purified by dialysis against running water, whereby it is obtained as a fawn-coloured powder which cannot be caused to crystallise. The presence of considerable amounts of dextrose in the sarsaparilla root considered in conjunction with the ready hydrolysis of the saponins by acids justifies the conclusion that the primary crystalline glucosides are partly changed by fermentative fission to amorphous, secondary glucosides; the contradictory results of previous investigations are probably due to the use of fresh or stored material. Saponin *B* is similarly purified by dialysis, which, however, does not remove a considerable content of aluminium, magnesium, and calcium, which are probably present in combination with galacturonic acid. These can be eliminated by solution of saponin *B* in alkali and precipitation with acid. The purified material then closely resembles saponin *A*. The composition of the products varies somewhat in different preparations; it appears that a loosely combined saccharide component is removed during the protracted extraction.

The saponins are hydrolysed by sulphuric acid (3—5%), whereby possibly galacturonic acid, glucose, pentoses, and methylpentoses are obtained. The presence of galactose, arabinose, or rhamnose could not be established. The sapogenin is freed from dark coloured impurities by solution in alcohol and precipitation with sodium ethoxide, whereby ultimately sarsapogenin, $C_{26}H_{42}O_3,H_2O$, slender, colourless needles, m. p. 183° (corr.), $[\alpha]_D^{17}$ −58·68° in absolute methyl alcohol, is isolated; the substance is identical with that

obtained by Power and Solway (T., 1914, **105**, 201) from Jamaica sarsaparilla. The substance contains one hydroxyl group, since it yields a monoacetate, colourless needles, m. p. 127°, $[\alpha]_D^{18}$ — 57·1° when dissolved in chloroform (Power and Solway, *loc. cit.*, give m. p. 137°). The acetyl compound is hydrolysed by barium hydroxide to a substance, $C_{26}H_{42}O_3,H_2O$, m. p. 122°; possibly racemisation or intramolecular transformation takes place. The *monobenzoyl* derivative forms colourless crystals, m. p. 124°. The presence of a carboxyl, carbonyl, alkyloxy-, or lactonic group could not be established in the usual manner. The remaining two oxygen atoms must therefore be present in the molecule as a stable bridge. Distillation with zinc dust and treatment of the distillate with steam gives a diterpene, $C_{10}H_{16}$, b. p. 204—206°/748 mm., (slight decomp.). H. W.

The Influence of Oxalic Acid on the Formation of Aniline-black. J. Piccard (*Helv. Chim. Acta*, 1923, **6**, 1029—1032).—The oxidation of a solution of aniline hydrochloride by sodium dichromate is accelerated about forty times by the addition of a small quantity of oxalic acid to the solution. The mechanism of the accelerating action has not been elucidated. The printing of Aniline-black on cotton or silk is facilitated by impregnating the material with aniline oxalate. [Cf. *B.*, 91.] E. H. R.

Platinum Oxide as a Catalyst in the Reduction of Organic Compounds. IV. Reduction of Furfuraldehyde and its Derivatives. W. E. Kaufmann and R. Adams (*J. Amer. Chem. Soc.*, 1923, **45**, 3029—3044; cf. A., 1922, ii, 558; 1923, ii, 310, 773).—When furfuraldehyde in alcoholic solution was reduced with hydrogen under 1—2 atm. pressure in the presence of platinum black, the first molecular equivalent of hydrogen absorbed gave a quantitative yield of furfuryl alcohol. The latter then reacted with hydrogen in four different ways to produce tetrahydrofurfuryl alcohol, *n*-amyl alcohol, pentane-αε-diol, and *pentane-αβ-diol*. The last-named substance, $CH_2Me{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$, boiled at 210·5—211·5°/751 mm., n_D^{19} 1·4412, d_{20}^{20} 0·9802. Its *diacetate* boiled at 219—220°/748 mm., n_D^{19} 1·4202, d_{20}^{20} 1·0148. The catalyst made from spectroscopically pure chloroplatinic acid was very inefficient and the addition of ferrous chloride increased the rate of reduction to a maximum beyond which the rate decreased rapidly. This decrease in the case of the reduction of the aldehyde group was much less than that of the subsequent reduction of the ethylene double bonds. After the absorption of each molecular equivalent of hydrogen the catalyst was reactivated by shaking with air or oxygen. Pyromucic acid gave tetrahydropyromucic acid, m. p. 21°, and ethyl pyromucate gave ethyl tetrahydropyromucate, b. p. 82°/11 mm., β-furylacrylic acid gave β-tetrahydrofurylpropionic acid, b. p. 135—137°/4 mm., furoin gave αβ-dihydroxy-αβ-ditetrahydrofurylethane, $C_4H_7O{\cdot}CH(OH){\cdot}CH(OH){\cdot}C_4H_7O$, furfurylideneacetone gave α-tetrahydrofurylbutan-γ-one and α-tetrahydrofurylbutan-γ-ol, b. p. 93—94°/2 mm., furfurylideneacetophenone gave γ-phenyl-

tetrahydrofurylpropan-γ-one, b. p. 153—154°/2 mm., and γ-phenyltetrahydrofurylpropan-γ-ol, b. p. 167—168°/2 mm. F. B.

Hydroxymethylfurfuraldehyde from Cellulose and its Derivatives. E. HEUSER and W. SCHOTT (*Cellulosechemie*, 1923, **4**, 85—89).—The hydroxymethylfurfuraldehyde which is formed on heating cellulose with 5% oxalic acid solution in an autoclave at 180° for half an hour has been shown to be identical with the isomeric modification described by Kiermayer. The following derivatives were prepared for this identification: Semicarbazone, m. p. 235—236°; phenylhydrazone, m. p. 140°; anhydride, m. p. 112°; *anti*-aldoxime, m. p. 76°; *syn*-aldoxime, m. p. 106°. The normal modification prepared by Erdmann from bromomethylfurfuraldehyde (from lævulose) gave a semicarbazone melting at 216°. This modification is converted into the isomeride by heating with 0·3% oxalic acid in a sealed tube. The hydroxymethylfurfuraldehyde is extracted from the filtered digestion liquor by shaking with ethyl acetate. The quantity of the aldehyde increases with the degree of hydrolysis of the cellulose; thus normal cotton yielded 15·36% of dextrose and only 0·82% of the aldehyde, viscose cellulose gave 63·21% of dextrose and 5·16% of the aldehyde, whilst hydrocellulose prepared from viscose according to the prescription of Knoevenagel and Busch yielded 68·47% of dextrose and 10·84% of hydroxymethylfurfuraldehyde. The presence of the aldehyde does not interfere with the estimation of the dextrose by the fermentation method. J. F. B.

Preparation of Chromans. L. CLAISEN (D.R.-P. 374142; from *Chem. Zentr.*, 1923, iv, 725; cf. Claisen and Tietze, A., 1921, i, 263—264).—Phenols are treated with butadienes in the presence of acid condensing reagents. Phenol and isoprene give 2 : 2-dimethylchroman. *p*-Cresol and isoprene give 2 : 2 : 6-*trimethylchroman*, a colourless oil with a strong odour, b. p. 244—244·5°; d_{15}^{15} 0·9920. *p*-Cresol and βγ-dimethylbutadiene give 2 : 2 : 3 : 6-tetramethylchroman, an oil, b. p. 257—258°; d_{15}^{15} 0·9813. *m*-Xylenol and βγ-dimethylbutadiene give a *pentamethylchroman*, b. p. 263—265°. G. W. R.

The Reduction of Chrysin. J. PICCARD and E. OPPENHEIM (*Helv. Chim. Acta*, 1923, **6**, 1009—1011).—Chrysin is reduced by magnesium in glacial acetic acid solution, forming a *compound* which is probably the hydrol of chrysin, $C_{15}H_{12}O_4$. It forms an amorphous, red powder, m. p. 210—226°, soluble in concentrated sulphuric acid and in alkalis with a yellow colour. It does not appear to be analogous to the violet substance obtained by Baeyer and Piccard by the reduction of dimethylpyrone (A., 1911, i, 901). E. H. R.

Dipyrylenes. F. ARNDT and P. NACHTWEY (*Ber.*, 1923, **56**, [*B*], 2406—2409).—When ethyl acetonedioxalate or ethyl chelidonate is boiled in benzene solution with phosphorus pentasulphide, a com-

pound is formed probably having the constitution *ethyl* 4 : 4′-*dipyrylene*-2 : 6 : 2′ : 6′-*tetracarboxylate*,

$$O<\begin{matrix}C(CO_2Et):CH\\C(CO_2Et):CH\end{matrix}>C:C<\begin{matrix}CH:C(CO_2Et)\\CH:C(CO_2Et)\end{matrix}>O.$$

It forms slender, cinnamon to carmine-red needles, m. p. 203—204°. In concentrated sulphuric acid, it dissolves with a deep red colour, changing slowly to deep green, but the ester is recovered from the green solution unchanged. 4 : 4′-*Dipyrylene*-2 : 6 : 2′ : 6′-*tetracarboxylic acid* forms a brownish-red, infusible powder; the *sodium* salt, $C_{14}H_4O_{10}Na_4,3H_2O$, is brownish-red. The formation of the above tetracarboxylate is preceded by that of an intermediate compound, *ethyl thiochelidonate*, $S:C<\begin{matrix}CH:C(CO_2Et)\\CH:C(CO_2Et)\end{matrix}>O$, bluish-green needles, m. p. 51°, which on heating decomposes into the ethyl dipyrylenetetracarboxylate and free sulphur. The thiochelidonate is conveniently isolated in the form of an additive compound with mercuric chloride, a deep yellow precipitate, m. p. 135—137°. E. H. R.

A Molecular Compound of Caffeine and Salicylic Acid. A. Regenbogen and N. Schoorl (*Pharm. Weekblad*, 1924, **61**, 34—36).—The melting-point curve for mixtures of the two substances shows the existence of an equimolecular compound with melting point about 135°. By fusing together equal molecular proportions of the components, and recrystallising from water, the compound is obtained as fine needles, m. p. 137°; it is unaltered by recrystallisation from chloroform, but decomposes in alcoholic solution. Its existence explains the solubility of caffeine in aqueous solutions of sodium salicylate. S. I. L.

Strychnos Alkaloids. XXXXI. Various Observations on Derivatives of Brucine. H. Leuchs, W. Gladkorn, and E. Hellriegel (*Ber.*, 1923, **56**, [*B*], 2472—2477).—Dihydrobrucinonic acid is decomposed by prolonged treatment with methyl-alcoholic ammonia at 100° into *iso*brucinolone, an amorphous substance, and aminodihydrobrucinolone.

The conversion of *iso*brucinolone by 5*N* nitric acid into the red quinone, $C_{19}H_{16}O_5N_2$, decomp. about 300°, is described in detail; the substance is reduced by sulphur dioxide to the corresponding *quinol*, $C_{19}H_{18}O_5N_2$, needles or prisms, m. p. 325—328° (decomp.) after darkening at 320°.

The oxidation of acetyl*iso*brucinolone dissolved in acetone by potassium permanganate does not take place smoothly and gives *dihydroxyacetyldihydroisobrucinolone*, $C_{23}H_{26}O_8N_2$, slender needles, m. p. 245°, as sole crystalline product in yield which does not exceed 12%. The acidic products of the oxidation are amorphous, but show the expected properties such as the red coloration with ferric chloride, the loss of carbon dioxide when heated, the decomposition by acidic hydrolysis into a hydrochloride (probably curbine hydrochloride in place of the expected *iso*curbine salt), and a nitrogen-free acid, apparently malonic acid. It therefore appears probable that *iso*-

brucinolone contains the same oxidisable group, $N{\cdot}CO{\cdot}CH_2{\cdot}CH{:}C{:}C_2$, as brucinolone-*b*, and yields a substance which is a semi-amide of malonic acid and a ketone. The study of the oxidation of *benzoyl-iso**brucinolone***, $C_{28}H_{26}O_6N_2$, very slender needles, m. p. 250° after darkening at 240° when rapidly heated, $[\alpha]_D^{16}$ +99° in glacial acetic acid solution, did not lead to more favourable results.

Brucinolic acid is converted by methyl-alcoholic ammonia at 100° into brucinolone, glycollic acid, and aminodihydrobrucinolone.

Brucinolone-*b* is converted by benzoic anhydride and sodium benzoate at 100° into *benzoylbrucinolone*-b, $C_{28}H_{26}O_6N_2$, prismatic aggregates, m. p. 235—236°, $[\alpha]_D^{16}$ −148° in glacial acetic acid solution, and by phosphorus pentachloride in the presence of chloroform at −20° and treatment of the product with ethyl alcohol into *brucinolone diethyl phosphate*, $PO(OEt)_2{\cdot}O{\cdot}C_{21}H_{21}O_4N_2$, large, colourless leaflets, m. p. 232—235°.

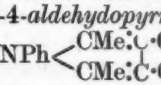
Brucinolone hydrate I and phenylcarbimide yield the compound $C_{28}H_{29}O_7N_3,H_2O$, coarse, domatic prisms, m. p. 191—192° (decomp.).

Dihydroxydihydroacetylbrucinolone is converted by acetic anhydride and anhydrous sodium acetate at 100° into *diacetyldihydroxydihydrobrucinolone*-b, $C_{25}H_{18}O_9N_2$, colourless crystals, m. p. about 280° (decomp.) after darkening and softening at 240°, $[\alpha]_D^{20}$ −149·2° in glacial acetic acid solution.

The oximation of *ON*-diacetylcurbin by a boiling alcoholic solution of hydroxylamine causes the loss of the *O*-acetyl group and formation of *N-acetylcurbinoxime*, $C_{20}H_{23}O_6N_2$, lustrous, rectangular prisms, m. p. 185—187°. The attempted isomerisation of the oxime by acetyl chloride at 100° leads to the production of *triacetylcurbinoxime*, $C_{24}H_{27}O_8N_3$, double pyramids, m. p. 275° (decomp.) after becoming yellow at 250°. H. W.

The Behaviour of Eucupine and Uric Acid Gels during Dialysis. The Distribution of Ions. P. Rona and W. B. Meyer (*Biochem. Z.*, 1923, **143**, 161—178).—In dialysing eucupine dihydrochloride ($C_{24}H_{34}O_2N_2,2HCl+2H_2O$) considerable membrane adsorption occurs. This is greater with collodion membranes than when Schleicher-Schüll shells are used, but diminishes with increasing acidity and disappears at p_H 4. The adsorption may be overcome by previously saturating the membrane with eucupine. Eucupine dihydrochloride forms a true solution. Eucupine acetate gel and lithium urate gel are partly colloidal (60%) and partly true solutions. In dialysing the urate gel, lithium and uric acid pass into the external fluid in equimolecular concentrations. The transition between supersaturated uric acid solution in lithium hydroxide and lithium urate gel is sharp, the former behaving as a true solution. On dialysing urate against potassium chloride, the potassium diffuses inwards and the lithium outwards in proportional amounts, whilst the external uric acid concentration diminishes with increasing amounts of potassium chloride. The system illustrates the unequal distribution of electrolytes on the two sides of a membrane with a non-diffusible colloidal ion on one side. J. P.

Some New *N*-Substituted Pyrrole-aldehydes; and Oxindole-aldehyde. HANS FISCHER and K. SMEYKAL (*Ber.*, 1923, 56, [*B*], 2368—2378).—The Gattermann aldehyde synthesis (cf. Fischer and Zerweck, A., 1922, i, 758) has been applied to the synthesis of a number of *N*-substituted pyrrole-aldehydes. *Ethyl* 1-*phenyl*-2 : 5-*dimethyl*-4-*aldehydopyrrole*-3-*carboxylate*,

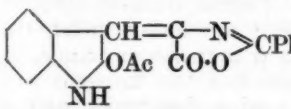


from ethyl 1-phenyl-2 : 5-dimethylpyrrole-3-carboxylate, forms colourless crystals, m. p. 82°; the free *acid* has m. p. 240°. The ethyl ester forms a *phenylhydrazone*, colourless crystals, m. p. 156—160°, and an *oxime*, m. p. 150°. *Ethyl* 1-p-*tolyl*-2 : 5-*dimethylpyrrole*-3-*carboxylate*, from *p*-toluidine, chloroacetone, and ethyl acetoacetate, forms colourless crystals, m. p. 55°; the free *acid* forms large crystals, m. p. 240°. By Gattermann's synthesis with hydrocyanic acid, the ester gives *ethyl* 1-p-*tolyl*-2 : 5-*dimethyl*-4-*aldehydopyrrole*-3-*carboxylate*, white, glistening crystals, m. p. 133°; the *phenylhydrazone* forms colourless, strongly refracting crystals, m. p. 92—96°; the *oxime* forms glistening leaflets, m. p. 138°, and the free *acid* forms colourless needles, m. p. 212°. The *semicarbazone* forms colourless needles, m. p. 240°. *Ethyl* 1 : 2 : 5-*trimethyl*-4-*aldehydopyrrole*-3-*carboxylate* forms long, white needles, m. p. 97°; the *phenylhydrazone* forms fine needles, m. p. 159—161°.

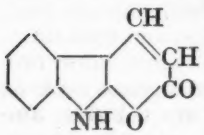
It has been suggested by Alessandri (A., 1915, i, 452) that a number of α-pyrrole-aldehydes have a hydroxymethylene structure, since they do not react with dihydroxyammonia, whilst the corresponding *N*-substituted α-pyrrole-aldehydes do so react. It is now found that neither ethyl 2 : 5-dimethyl-4-aldehydopyrrole-3-carboxylate, ethyl 2 : 4-dimethyl-3-aldehydopyrrole-5-carboxylate, nor the new *N*-substituted pyrrole-aldehydes reacts with benzenesulphohydroxamic acid. Probably all are true aldehydes, although not giving all the typical aldehyde reactions. There may be an equilibrium between the two forms.

The *N*-substituted pyrrole-aldehydes react with nitroacetic acid, with loss of carbon dioxide, forming nitrovinylpyrroles, and with ethyl cyanoacetate to give substituted vinylpyrroles. *Ethyl* 1-*phenyl*-2 : 5-*dimethyl*-4-*nitrovinylpyrrole*-3-*carboxylate* forms yellow crystals, m. p. 130—132°; the corresponding 1-p-*tolyl* compound forms glistening yellow leaflets, m. p. 125—133°. *Ethyl* 2 : 5-*dimethyl*-4-[ω-*cyano*-ω-*carbethoxyvinyl*]*pyrrole*-3-*carboxylate* forms white needles, m. p. 139°. The 1-*phenyl* derivative forms colourless needles, m. p. 110°, and the 1-p-*tolyl* derivative, white needles, m. p. 121°.

Oxindole-3-aldehyde condenses with hippuric acid to form an *azlactone* which forms an *acetyl* derivative, stout prisms, m. p. 185°. It may have the annexed formula. Hydrolysis experiments failed to give an unsaturated acid, but merely removed the acetyl group, which may therefore be attached to the nitrogen. The hydrolysed product had m. p. 260°. *N*-Methyloxindole-



3-aldehyde also formed an *acetylazlactone*, glistening red needles, m. p. 205°, which when hydrolysed gave the *azlactone*, red needles, m. p. 287°. The acetyl group cannot, in this case, be attached to nitrogen, but it is still doubtful what positions are occupied in the molecule by the acetyl and benzoyl groups. Oxindole-3-aldehyde gives by Perkin's reaction a *compound*, $C_{11}H_7O_2N$, yellow tablets, m. p. 247°, probably having the annexed coumarin formula. It forms a crystalline, molecular compound with 1 mol. of aniline, m. p. 160°. Oxindole-3-aldehyde forms an *acetyl* derivative, m. p. 185°, and a *benzoyl* derivative, m. p. 196°; *N*-methyloxindole-3-aldehyde gives an *acetyl* derivative, yellow needles, m. p. 135°, and a *benzoyl* derivative, greenish-yellow needles, m. p. 147°. E. H. R.



A New Synthesis of Hæmatic Acid. W. KÜSTER and H. MAURER (*Ber.*, 1923, **56**, [*B*], 2478—2481).—A new synthesis of hæmatic acid starting from ethyl 4-aldehydo-3 : 5-dimethylpyrrole-2-carboxylate (cf. Fischer, Weiss, and Schubert, A., 1923, i, 703) is recorded. The preliminary work is carried out with the more accessible ethyl 2-aldehydo-3 : 5-dimethylpyrrole-4-carboxylate.

Ethyl 2-aldehydo-3 : 5-dimethylpyrrole-4-carboxylate is condensed with ethyl malonate in the presence of acetic anhydride at a temperature not exceeding 150° to *ethyl* 4-*carbethoxy*-3 : 5-*dimethylpyrrole*-2-*vinyl*-ωω-*dicarboxylate*, small, yellow needles, m. p. 86°, which is reduced and partly hydrolysed by sodium amalgam to 4-*carbethoxy*-3 : 5-*dimethylpyrrole*-2-*ethyl*-ωω-*dicarboxylic acid*, $C_{13}H_{17}O_6N$, a colourless powder, m. p. 218°. The acid loses carbon dioxide when heated and passes into 4-*carbethoxy*-3 : 5-*dimethylpyrrole*-2-*propionic acid*, slender, colourless needles or rectangular prisms, m. p. 120°; the *iron* and *copper* salts are described.

Ethyl 4-aldehydo-3 : 5-dimethylpyrrole-2-carboxylate and ethyl malonate yield *ethyl* 2-*carbethoxy*-3 : 5-*dimethylpyrrole*-4-*vinyl*-ωω-*dicarboxylate*, $\begin{matrix}CO_2Et\cdot C:CMe\\ \quad\quad\vdots\\ HN\cdot CMe\end{matrix}\!\!>C\cdot CH:C(CO_2Et)_2$, colourless needles, m. p. 99—100°, which is transformed by sodium amalgam into 2-*carbethoxy*-3 : 5-*dimethylpyrrole*-4-*ethyl*-ωω-*dicarboxylic acid*,

$$\begin{matrix}CO_2Et\cdot C\cdot CMe\\ \quad\quad\vdots\\ HN\cdot CMe\end{matrix}\!\!>C\cdot CH_2\cdot CH(CO_2H)_2,$$

colourless leaflets or thick needles, m. p. 184—185° (decomp.); the *ferric* and *calcium* salts are described. The acid passes when heated above its melting point into 2-*carbethoxy*-3 : 5-*dimethylpyrrole*-4-*propionic acid*, $\begin{matrix}CO_2Et\cdot C:CMe\\ \quad\quad\vdots\\ HN\cdot CMe\end{matrix}\!\!>C\cdot CH_2\cdot CH_2\cdot CO_2H$, colourless leaflets, m. p. 152°, the *silver* and *ferric* salts of which are described. Oxidation of 2-carbethoxy-3 : 5-dimethylpyrrole-4-propionic acid by chromic acid in glacial acetic acid solution gives the imide of hæmatic acid, $\begin{matrix}CO\cdot CMe\\ \quad\quad\vdots\\ NH-CO\end{matrix}\!\!>C\cdot CH_2\cdot CH_2\cdot CO_2H$, which is characterised by hydrolysis by means of barium hydroxide to the anhydride, m. p. 97°. H. W.

Pyrroles. F. Angelico and F. Monforte (*Gazzetta*, 1923, **53**, 795—800).—It has been shown (A., 1905, i, 938; 1909, i, 122; 1910, i, 444; 1911, i, 1032) that, when boiled with dilute sulphuric acid, diazotriphenylpyrrole yields azinetriphenylpyrrole. Further experiments show that diazotriphenylpyrrole is a highly stable compound and is not altered by iodine, sodium thiosulphate, alcohol, or organic acids. With mineral acids, it yields salts, and with nitric acid, also nitro-derivatives. Energetic oxidising agents cause profound decomposition of the molecule. Reducing agents such as zinc dust and acetic acid, zinc dust and ammonium chloride, ammonium sulphide, or hydroxylamine convert it into the amino-compound, whilst by the action of hydrogen in presence of palladium black it is converted into ammonia and triphenylpyrroline; the latter reduction resembles that of diphenyldiazomethane, which yields principally diphenylmethane and nitrogen (cf. Staudinger, Gaule, and Siegwart, A., 1921, i, 323), but it has not been found possible to convert diazotriphenylpyrrole by reduction into the corresponding hydrazine, although this is possible with certain of the aliphatic diazo-compounds. Like both the corresponding indole derivative and various aromatic diazo-compounds, diazotriphenylpyrrole is extremely sensitive to the action of light, this causing it to darken and to undergo transformation into a compound which has a lower melting point and a diminished proportion of nitrogen, but has not yet been identified.

2 : 5-Diphenylpyrrole-3-carboxylic acid readily yields the corresponding oximino-compound, but in the passage to the amine the carboxyl group is eliminated in the cold. Hence, to prepare the diazo-compound it is not necessary to convert the carboxylic acid into 2 : 3-diphenylpyrrole itself.

The *compound*, $C_{22}H_{13}O_4N_5$, obtained by the action of concentrated nitric acid in the cold on diazotriphenylpyrrole, forms crystals, m. p. 185°. If a mixture of nitric and sulphuric acids is employed, the product forms crystals, m. p. 110°, and contains rather more nitrogen than is represented by the above formula.

Oximino-2 : 5-diphenylpyrrole-3-carboxylic acid, $C_{17}H_{13}O_3N_2$, crystallises in golden-yellow scales, m. p. 212° (decomp.), and yields aminodiphenylpyrrole, m. p. 186°, when reduced in alcoholic solution by means of ammonium sulphide. T. H. P.

A Complex Silver Fluoride. A. Burada (*Ann. Sci. Univ. Jassy*, 1923, **12**, 33—34; from *Chem. Zentr.*, 1923, iii, 1225).—By addition to a solution of silver fluoride of the theoretical quantity of pyridine and evaporation in a vacuum over sulphuric acid with exclusion of light, a *compound* is obtained of the composition $AgF,2C_5H_5N,5H_2O$; it forms colourless, transparent crystals, unstable in air and light. When heated, it is decomposed completely leaving a residue of metallic silver. G. W. R.

Preparation of Amino-substitution Products of Pyridine and Quinoline Series. A. E. Tschitschibabin (D.R.-P. 374291; from *Chem. Zentr.*, 1923, iv, 725; cf., A., 1923, i, 1121).—Pyridine,

quinoline, their homologues or derivatives, or other bases containing the pyridine ring, or natural organic bases such as alkaloids, are treated in the absence or presence of indifferent solvents, with sodamide, or compounds of the general formula R·NHNa, where R=aryl, alkyl, or a heterocyclic basic residue such as pyridyl or quinolyl, or mixtures of sodium with primary amines. After treatment of the products of reaction with water, the amino-compounds obtained are separated by distillation or other suitable method. The reactions are shown by the following equations: (i) $C_5H_5N+NH_2Na=C_5H_4N\cdot NHNa+H_2$, (ii) $C_5H_4N\cdot NHNa+H_2O=C_5H_4N\cdot NH_2+NaOH$, (iii) $C_5H_4N\cdot NHNa+C_5H_5N=(C_5H_4N)_2NNa+H_2$, (iv) $(C_5H_4N)_2NNa+H_2O=(C_5H_4N)_2NH+NaOH$. The amino-group goes into the ortho-position relatively to the pyridine nitrogen. 2-Aminopyridine has m. p. 56°. Other compounds mentioned are: 6-*amino*-2-*methylpyridine*, a deliquescent substance, m. p. 36·5°, b. p. 208—209°; 2-aminoquinoline, leaflets, m. p. 129°; 2 : 6-diamino-pyridine, obtained by heating pyridine and sodamide in the presence of vaseline oil at 125° and then at 180°, leaflets, m. p. 121·5°; 2-anilinopyridine, from pyridine and sodium anilide, crystals, m. p. 108°; 2 : 2-dipyridylamine, small needles, m. p. 95° (stable form), m. p. 86—87° (labile form); *aminonicotine*, crystals, m. p. 125—126°; 6-*amino*-2-*hydroxypyridine*; 2 : 6-diaminopyridine couples with aromatic diazo-compounds with formation of colouring matters. Nitration of 2-aminopyridine yields 5-*nitro*-2-*aminopyridine*, yellow leaflets, m. p. 188°, and 3-*nitro*-2-*aminopyridine*, yellow needles, m. p. 164°. From 5-nitro-2-aminopyridine, 2 : 5-*diaminopyridine* is obtained by reduction. G. W. R.

The Synthesis of Ricinine. E. Späth and G. Koller (*Ber.*, 1923, **56**, [*B*], 2454—2460).—The constitution assigned previously to ricinine (Späth and Koller, A., 1923, i, 594) is confirmed by its synthesis from 4-chloroquinoline.

Ricinidine is converted by a molecular proportion of bromine in aqueous solution into a mixture of bromo-compounds which is transformed by boiling potassium carbonate solution into a product, m. p. 287°; it is not identical with ricinic acid.

4-Hydroxy-1-methylpyrid-2-one reacts with a molecular proportion of bromine in aqueous solution to give a homogeneous bromo-derivative, m. p. 219—219·5°; attempts to replace the halogen atom of this compound by the cyano-group were unsuccessful.

4-Chloroquinoline is oxidised by potassium permanganate in boiling aqueous solution in the presence of carbon dioxide to 4-*chloropyridine*-2 : 3-*dicarboxylic acid*, coarse, pale yellow crystals, m. p. 173° (decomp.) when rapidly heated. The acid is fairly smoothly converted by acetic anhydride into the corresponding *anhydride*, colourless needles, m. p. 200—202° (slight decomp.), in an evacuated tube, which is converted by ammonia in the presence of benzene into 4-*chloro*-2-*carbamidopyridine*-3-*carboxylic acid*, lustrous needles, m. p. 148—150° (decomp.) when rapidly heated. The latter acid is converted by bromine and potassium hydroxide into

4-chloro-2-aminopyridine-3-carboxylic acid, slender, colourless crystals, decomp. 173°, which is conveniently purified through the *ammonium* salt; it is transformed by nitrous acid in sulphuric acid solution into *4-chloro-2-hydroxypyridine-3-carboxylic acid*, colourless needles, m. p. 220° (decomp.). The constitution of the hydroxy-acid is established by its conversion by hydrogen in the presence of palladised barium sulphate into the previously described 2-hydroxy-pyridine-3-carboxylic acid, and thence into 2-hydroxypyridine. Attempts to effect the complete methylation of 4-chloro-2-hydroxy-pyridine-3-carboxylic acid with diazomethane or by the action of methyl iodide on the di-silver salt were not successful. The acid is therefore converted by the successive action of phosphoryl chloride and phosphorus pentachloride and of ammonia into 2 : 4-*dichloropyridine-3-carboxylamide*, colourless crystals, m. p. 181—182° (decomp.), which is transformed by phosphoryl chloride into 2 : 4-*dichloro-3-cyanopyridine*, m. p. 112—113°. When treated with boiling methyl-alcoholic sodium methoxide solution, both chlorine atoms are replaced by methoxy-groups with the production of *3-cyano-2 : 4-dimethoxypyridine*, coarse, colourless crystals, m. p. 145—146°, and a substance, m. p. 221—222°, which has not been examined completely. The conversion of 3-cyano-2 : 4-dimethoxy-pyridine into ricinine, m. p. 197°, could not be effected by heating it at 300°, but occurs readily when it is treated with methyl iodide in an evacuated tube at 120—130°. H. W.

Keto-anils. V. The Formation of Quinolines from Ketones and Aromatic Amines. E. KNOEVENAGEL [with E. WAGNER and H. BÄHR] (*Ber.*, 1923, **56**, [*B*], 2414—2418).—The production of derivatives of quinoline from aniline and ketones or aldehydes has been ascribed to the intermediate formation of alkylidene ketones and aldols, respectively. Evidence is now brought forward, however, in favour of the view that in the formation of 2-methyl- or 2 : 4-dimethyl-quinolines an alkylidene- or a ketylidene-amine derivative is essential which passes into a dimeride and thence into a quinoline compound. It is quite possible that the formation of aldols from aldehydes, ketones, or mixtures occurs under the condensing influence of hydrogen chloride, but compounds of this type are decomposed by aromatic amines with formation of alkylidene- or ketylidene-amines and liberation of the equivalent quantity of aldehyde or ketone.

The preparation of methyl*iso*propenylaniline (cf. Bähr, A., 1922, i, 750) from acetoneanil and methyl sulphate is described. It is converted by cyanoacetic or chloroacetic acid (but not by the dichloro- or trichloro-acid) into dimeric methyl*iso*propenylaniline, m. p. 148°, which is identical with the by-product isolated by Bähr (*loc. cit.*) during the preparation of methyl*iso*propenylaniline by means of methyl iodide. The dimeride is transformed by dry hydrogen chloride at 180—200° into 2 : 4-dimethylquinoline.

The action of mesityl oxide on aniline in the presence of a little iodine leads to the formation of acetoneanil and acetone. The condensation of mesityl oxide with aniline hydrochloride at 180°

takes place with liberation of methane, and not of methyl chloride as stated by Beyer.

In the presence of iodine, phorone and mesityl oxide yield acetone, unchanged phorone, and acetoneanil. In the absence of iodine, condensation does not appear to occur. Under the influence of iodine and water, phorone does not appear to yield acetone. H. W.

Amino-alcohols of the Quinoline Series. SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pats. 98482, 98712, and 98713; from *Chem. Zentr.*, 1923, iv, 829—830; cf. A., 1923, i, 148, 149).—6-Ethoxy-2-phenyl-4-quinolyl methyl ketone is halogenated in the methyl group and the resultant halogen derivative allowed to react with dimethylamine, diethylamine, or piperidine. The *N*-substituted 6-ethoxy-2-phenyl-4-quinolylamino-ethanone thereby obtained is then reduced to the corresponding aminoalcohol. 6-*Ethoxy*-2-*phenyl*-4-*quinolyl methyl ketone* forms yellow crystals, m. p. 107°; the *hydrochloride*, yellow crystals, has m. p. about 220° (decomp.). It is obtained by condensation of ethyl 6-ethoxy-2-phenylquinoline-4-carboxylate with ethyl acetate and elimination of carbon dioxide from the *ethyl* 6-*ethoxy*-2-*phenylquinoline*-4-*acetate*, m. p. 98—99°, thereby formed, or from 4-cyano-6-ethoxy-2-phenylquinoline by the Grignard reaction. By acting on the above-mentioned ketone with bromine in hydrobromic acid solution, 6-*ethoxy*-2-*phenyl*-4-*quinolyl bromomethyl ketone hydrochloride*, yellow crystals, m. p. 207° (decomp.), is obtained; the free *ketone* forms yellow crystals, m. p. 129°. By acting on the bromomethyl ketone with dimethylamine, 6-*ethoxy*-2-*phenyl*-4-*quinolyl dimethylaminomethyl ketone*, $OEt\cdot C_9NH_4Ph\cdot CO\cdot CH_2\cdot NMe_2$, is obtained as the *hydrobromide*, yellow crystals, m. p. 230° (decomp.). The latter by reduction with hydrogen in the presence of a catalyst gives 6-*ethoxy*-2-*phenylquinolyl*-4-*dimethylaminoethanol*,

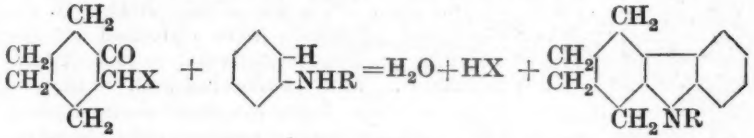
$$OEt\cdot C_9NH_4Ph\cdot CH(OH)\cdot CH_2\cdot NMe_2,$$

which forms colourless, rosette-like needles, m. p. 95°; the *dihydrochloride* forms light yellow crystals, m. p. about 210° (decomp.). 6-*Ethoxy*-2-*phenyl*-4-*quinolyl diethylaminomethyl ketone monohydrobromide*, yellow crystals, m. p. about 210° (decomp.), 6-*ethoxy*-2-*phenyl*-4-*quinolyl piperidinomethyl ketone*, a yellow powder, m. p. 82° (indef.), the *hydrochloride*, m. p. about 260° (decomp.), and the *hydrobromide*, m. p. 235—240° (decomp.), of the latter are similarly obtained. The corresponding amino-alcohols are obtained by reduction. 6-*Ethoxy*-2-*phenyl*-4-*quinolyldiethylaminoethanol* forms crystals, m. p. 89° after softening; the *dihydrochloride*, yellow crystals, has m. p. 205°. 6-*Ethoxy*-2-*phenyl*-4-*quinolylpiperidinoethanol* forms colourless crystals, m. p. 110°; the *dihydrochloride*, yellow crystals, has m. p. 218°. G. W. R.

Preparation of a 2-Phenylquinolinedicarboxylic Acid. NEUMANN & CO. and J. ZELTNER (D.R.-P. 373285; from *Chem. Zentr.*, 1923, iv, 664—665).—Acetophenone-*o*-carboxylic acid, prepared, for example, from phthalic anhydride, acetic anhydride, and potassium acetate, is condensed with isatin by heating in the presence of potassium hydroxide solution at 100°. On acidifying,

2-phenylquinoline-4 : 7-dicarboxylic acid is obtained; it is a yellow, crystalline powder, m. p. 200°. G. W. R.

Preparation of Tetrahydrocarbazoles. CHEMISCHE FABRIKEN VORM. WEILER-TER MEER (D.R.-P. 374098; from *Chem. Zentr.*, 1923, iv, 724).—2-Halogen*cyclo*hexanones are condensed with primary or secondary aromatic amines, unsubstituted in the ortho-position to the amino-group. The reaction takes place in the presence of such basic substances as potassium carbonate or anhydrous potassium acetate, and is represented by



The following compounds are mentioned: tetrahydrocarbazole, from aniline and chloro*cyclo*hexanone; *3-methyltetrahydrocarbazole*, m. p. 142°, from *o*-toluidine and chloro*cyclo*hexanone; *1-methyltetrahydrocarbazole*, m. p. 98°, from *p*-toluidine and chloro*cyclo*hexanone; *N-ethyltetrahydrocarbazole*, a viscous oil, b. p. 220°/40 mm., from ethylaniline and 1 : 2-chloro*cyclo*hexanone. G. W. R.

Preparation of Aromatic α-Ketonic Acids. R. SÖDERQUIST (*Svensk Kem. Tidskr.*, 1922, **34**, 189—192; from *Chem. Zentr.*, 1923, iii, 1082—1083).—Aromatic α-ketonic acids are prepared by condensation of aldehydes with 4-oxo-2-thio-3-phenyloxazolidine. After oxidation and fission of the substituted oxazolidine ring, aromatic α-ketonic acids are obtained together with phenyl thiocarbimide. The condensation proceeds readily in acetic anhydride solution in the presence of anhydrous sodium acetate. Fission of the aryldihydroxyoxazolidines obtained by oxidation, takes place at the ordinary temperature on treatment with sodium ethoxide. The compounds may be separated by fractionation or by way of their hydrogen sulphite compounds. Anhydro-acids are also obtained from the elimination of a molecule of water from two ketonic acid molecules. *4-Oxo-2-thio-3-phenyl-5-benzylideneoxazolidine*, from benzaldehyde and 4-oxo-2-thio-3-phenyloxazolidine, has m. p. 185—185·5°. On oxidation, it yields *2 : 4-dihydroxy-3-phenyl-5-benzylideneoxazolidine*, m. p. 238—239°, whilst among the products of reaction with sodium ethoxide is phenylpyruvic acid. Other compounds mentioned are: *4-oxo-2-thio-3-phenyl-5-o-chlorobenzylideneoxazolidine*, fine thread-like or prismatic crystals, m. p. 141·5°; *2 : 4-dihydroxy-3-phenyl-5-o-chlorobenzylideneoxazolidine*, m. p. 152°; *o-chlorophenylpyruvic acid*, colourless leaflets, m. p. 145° (m. p. 152—152·5° when heated quickly); *semicarbazone* of the latter, m. p. 167·5°; *phenylhydrazone*, m. p. 141°; *4-oxo-2-thio-3-phenyl-5-m-chlorobenzylideneoxazolidine*, light yellow prisms, m. p. 192°; *m-chlorophenylpyruvic acid*, prisms; semicarbazone of the latter, m. p. 176°; *phenylhydrazone*, m. p. 141°; *4-oxo-2-thio-3-phenyl-5-p-chlorobenzylideneoxazolidine*, m. p. 237—237·5°; *p-chlorophenylpyruvic acid*, platelets; *semicarbazone* of the latter,

m. p. 184°; *phenylhydrazone*, m. p. 164°; 4-*oxo*-2-*thio*-3-*phenyl*-5-(3′ : 4′)*methylenedioxybenzylideneoxazolidine*, m. p. 240°; 2 : 4-*methylenedioxyphenylpyruvic acid*, colourless leaflets; *semicarbazone* of the latter, m. p. 197°; *phenylhydrazone*, m. p. 144°; 4-*oxo*-2-*thio*-3-*phenyl*-5-m-*nitrobenzylideneoxazolidine*, m. p. 207°; 4-*oxo*-2-*thio*-3-*phenyl*-5-o-*acetoxybenzylideneoxazolidine*, yellow prisms, m. p. 162·5—163°. G. W. R.

Action of Hydroxylamine and of Hydrazine on the Aryl Monothioamides of Carbethoxyethylmalonate. D. E. Worrall (*J. Amer. Chem. Soc.*, 1923, **45**, 3092—3095; cf. A., 1922, i, 874).—*iso*Oxazoles and pyrazoles were obtained by the action of hydroxylamine and hydrazine, respectively, on carbethoxyethylmalonate monothioamides. Thus carbethoxyethylmalonate monothioanilide gave *ethyl* 3-*anilino*-5-*oxo*-isooxazole-4-*carboxylate*, small needles, m. p. 166°, and the corresponding *pyrazole* ester, fluffy, white needles, m. p. 194—195°. *Ethyl* 3-o-*toluidino*-5-isooxazole-4-*carboxylate*, flat needles, m. p. 165—167° (decomp.), and the corresponding *pyrazole* ester, white needles, m. p. 215° (decomp.); *ethyl* 3-p-*toluidino*-5-*oxo*isooxazole-4-*carboxylate*, needles and plates, m. p. 172—173° (decomp.), and the corresponding *pyrazole* ester, feathery needles, decomp. above 200°; *ethyl* 3-p-*bromoanilino*-5-*oxo*isooxazole-4-*carboxylate*, slender needles, m. p. 163—170° (decomp.), and the corresponding *pyrazole* ester, needles, m. p. 217°, were obtained. F. B.

4′-Amino-1-phenyl-5-methylbenzthiazole and its Bromination in Glacial Acetic Acid. The Dibromo-product of Gatterman. The Fluorescence of some Benzthiazoles. R. F. Hunter (*Chem. News*, 1923, **127**, 385—386).—An alcoholic solution of dehydrothiotoluidine (4′-amino-1-phenyl-5-methylbenzthiazole) exhibits a green fluorescence in the light of a mercury lamp; its dibromide shows a blue fluorescence in glacial acetic acid solution, and the acetyl derivative is also strongly fluorescent. The dibromide is decomposed by nitrous acid and consequently cannot be diazotised. E. H. R.

Absorption Colours of the Second Order. J. Piccard and F. de Montmollin (*Helv. Chim. Acta*, 1923, **6**, 1011—1019).—It was shown previously that *meri*-quinonoid salts of tetraphenylbenzidine have a yellow colour of the second order (A., 1913, i, 895). It is now shown that Nietzki's rule also applies to such second order colours; the second absorption band can be moved further into the visible spectrum by increasing the molecular weight, changing the colour of the compound from yellow to red. This has been demonstrated by preparing a *meri*-quinonoid salt of diphenyldi-*p*-diphenylylbenzidine, $C_6H_4Ph{\cdot}NPh{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NPh{\cdot}C_6H_4Ph$. *Diphenyl*-p-*diphenylylamine*, $C_6H_4Ph{\cdot}NPh_2$, is formed by heating diphenylamine with *p*-iododiphenyl in nitrobenzene in presence of potassium carbonate and a little copper; it forms long, nearly colourless crystals, m. p. 114°. It forms a yellowish-green compound with chloranil, and gives a greenish-blue coloration with concentrated

sulphuric acid. When oxidised in glacial acetic acid with sodium dichromate, it gives a red colour, changing to green; the green solution is reduced with zinc dust and from the diluted solution *diphenyldidiphenylylbenzidine* can be extracted with chloroform, in 20% yield. It forms a brown powder, m. p. 135—140°. The same substance can be obtained in an impure form by condensing *s*-diphenylbenzidine with *p*-iododiphenyl. All solutions of the compound show a strong violet fluorescence which is excited by ultra-violet light at the limit of the visible spectrum. This benzidine derivative is oxidised by sodium dichromate in glacial acetic acid solution into a *meri*-quinonoid salt which can be precipitated by picric acid as meri-*diphenyldi*-p-*diphenylyldiphenoquinonedi-immonium picrate*, a red powder. Further oxidation gives the green *holo*-quinonoid salt. E. H. R.

Additive Reactions of Thiocyanogen. H. P. KAUFMANN and J. LIEPE (*Ber.*, 1923, **56**, [*B*], 2514—2520).—Attempts have been made to estimate enols by titration with solutions of thiocyanogen in the hope of thereby avoiding secondary disturbances such as may be caused by the liberated hydrogen bromide in Meyer's bromine titration method. It is found, however, that the reagent can be applied only under definite conditions; in general applicability and rapidity of execution, the method is not equal to Meyer's process. Quantitative experiments with solutions of thiocyanogen are rendered very difficult on account of the ease with which it becomes polymerised, particularly on exposure to sunlight or to an elevated temperature.

Thiocyanogen reacts with antipyrine in the presence of chloroform to give a mixture of *antipyrine thiocyanate*, colourless, lustrous needles, m. p. 125° (which is also obtained from antipyrine sulphate and potassium thiocyanate) and 4-*thiocyano*-1-*phenyl*-2 : 3-*dimethyl-pyrazol*-5-*one*, $\begin{matrix}C(SCN)\cdot CO\\ \|\\ CMe{-}NMe\end{matrix}\!>\!NPh$, colourless crystals, m. p. 147—148°; the constitution of the latter substance follows from its preparation from 4-bromoantipyrine and potassium thiocyanate in boiling aqueous solution. 4-*Thiocyanoantipyrine thiocyanate* has m. p. 84°. 4-Thiocyanoantipyrine is very readily hydrolysed by alkali hydroxide to potassium cyanide, potassium cyanate, and *bis*-1-*phenyl*-2 : 3-*dimethyl*-5-*pyrazolonyl* 4-*disulphide*,

$$\begin{matrix}NPh{-}CO\\ |\\ NMe\cdot CMe\end{matrix}\!>\!CS\cdot SC\!<\!\begin{matrix}CO{-}NPh\\ |\\ CMe\cdot NMe\end{matrix}$$

very pale yellow, hexagonal plates, m. p. 256°; the compound can also be prepared by means of aqueous alcohol. 4-Thiocyanoantipyrine is reduced by zinc and hydrochloric acid in the presence of alcohol to the additive *compound* of zinc chloride and 4-thiolantipyrine, $C_{11}H_{12}ON_2S,ZnCl_2$, a white precipitate from which the thiol could not be isolated.

[With M. THOMAS.]—Addition and substitution of free thiocyanogen occur much more slowly than in the case of bromine. Thus ethyl hydrocollidinedicarboxylate reacts with seven atomic proportions of chlorine and four of bromine, but not with iodine; with

thiocyanogen, it gives a *di-thiocyano*-derivative, $C_{16}H_{19}O_4N_3S_2$, m. p. 115° (decomp.). *Ethyl collidinedicarboxylate thiocyanate* crystallises in colourless, monoclinic plates, m. p. 133°.

[With M. THOMAS.]—Reactions with free cyanogen depend greatly on the solvent used, addition occurring particularly rapidly in the presence of nitromethane (as example of a solvent of high dissociating power). The action of sunlight and of certain catalysts, notably iron, is advantageous. Thus, whereas salicylic acid is indifferent towards thiocyanogen under the usual conditions, it is converted in nitromethane solution in the presence of iron powder into *2-hydroxy-5-thiocyanobenzoic acid*, monoclinic leaflets, m. p. 167—168°.

H. W.

New Methods of Splitting Pyrimidines. II. Decomposition of Pyrimidines by means of Ferrous Salts. M. H. PFALTZ and O. BAUDISCH (*J. Amer. Chem. Soc.*, 1923, **45**, 2972—2980; cf. A., 1921, ii, 337).—The splitting of pyrimidines under conditions closely resembling those in the metabolism of plants and animals was accomplished by the action of the system ferrous sulphate–sodium hydrogen carbonate–air and the system sodium pentacyanoaquoferroate–oxygen or air (A., 1900, i, 591) on uracil and thymine. In each case the pyrimidine ring was partly hydrolysed, with the formation of highly coloured intermediate substances which were completely hydrolysed by warm sodium hydrogen carbonate with the production of carbamide. The action was retarded by hydrogenation of the pyrimidine ring as in hydrouracil and by the presence of a methyl group in the 5-position as in thymine, and by the addition of any substance possessing a strong affinity for iron, *e.g.*, ammonia, potassium cyanide. F. B.

5-Benzoylbarbituric Acids. H. BILTZ and T. KÖHLER (*Ber.*, 1923, **56**, [*B*], 2482—2489).—In continuation of the work on 5-acylbarbituric acid (cf. Biltz and Wittek, A., 1921, i, 454), 5-benzoylbarbituric acid has been examined in detail. The position of the benzoyl group is placed beyond doubt by the observed ketonic properties of the compound, by the existence of similar derivatives of 1 : 3-dimethyl- and 1 : 3-diethyl-barbituric acids, and by the inability of alkalis to effect hydrolysis.

5-Benzoylbarbituric acid, $CO<^{NH\cdot CO}_{NH\cdot CO}>CHBz$, pale yellow aggregates of prisms, m. p. 275° (decomp.), is prepared by heating barbituric acid with benzoic anhydride at 175° during five hours; it cannot be prepared from barbituric acid, benzoyl chloride, and sodium hydroxide or from barbituric and benzoic acids. The *potassium* salt, rhombic leaflets, decomp. about 315°, is described. It is stable towards sodium hydroxide solution or concentrated hydrochloric acid. It is decomposed by hot fuming nitric acid into alloxan and benzoic or nitrobenzoic acids, and by bromine in aqueous solution at the atmospheric temperature into benzoic and 5 : 5-dibromobarbituric acids. It gives a *hydrazone*, $C_{11}H_{10}O_3N_4$, slender, pale yellow needles, decomp. 260°, and a *phenylhydrazone*, $C_{17}H_{14}O_3N_4$, small, pale yellow needles, decomp. 218°; a semi-

carbazone could not be obtained. It is decomposed by thiosemicarbazide in boiling aqueous-alcoholic solution into barbituric acid and 2-amino-5-phenylthiodiazole (cf. Young and Eyre, T., 1901, **79**, 57); 5-acetylbarbituric acid yields, in a similar manner, barbituric acid and 5-amino-2-methylthiodiazole. The action of hydroxylamine on 5-benzoylbarbituric acid in boiling alcoholic solution gives a *substance*, colourless, lustrous, hexagonal platelets, m. p. 261°, which is regarded as the oxime of 5-amino-5-benzoylbarbituric acid, $CO<^{NH\cdot CO}_{NH\cdot CO}>C(NH_2)\cdot CPh{:}N\cdot OH$; it is converted by hot, concentrated nitric acid into alloxan, by highly concentrated hydriodic acid into benzoylbarbituric acid, and by bromine water into alloxan and benzaldehyde. 5-Benzoylbarbituric acid is converted by sodium hydroxide and methyl sulphate into the *methyl ether* of the enolic form of 5-benzoylbarbituric acid, $CO<^{NH\text{——}CO}_{NH\cdot C(OMe)}>CBz$, colourless, lustrous prisms, decomp. 105°; the corresponding *phenylhydrazone*, $C_{18}H_{16}O_3N_4$, decomp. 225°, is described. The ethylation of 5-benzoylbarbituric acid could not be effected by ethyl sulphate or ethyl bromide, magnesium oxide, and carbon tetrachloride at 140°.

1-Methylbarbituric acid and benzoic anhydride react at 130—140° to give *5-benzoyl-1-methylbarbituric acid*, small, pale brown prisms, decomp. 225° (*phenylhydrazone*, slender, yellow needles, decomp. 205°). *5-Benzoyl-1-ethylbarbituric acid*, flattened prisms, m. p. 205° (decomp.), and its *phenylhydrazone*, slender needles, decomp. 190° after darkening at 175°, are described. 1 : 3-Dimethylbarbituric acid reacts with benzoic anhydride at 130°, but the expected 5-benzoyl-1 : 3-dimethylbarbituric acid could not be isolated from the product of the reaction in the homogeneous condition; it is characterised as the *phenylhydrazone*, $C_{19}H_{18}O_3N_4$, colourless, quadratic leaflets, decomp. 218°. 5-Benzoyl-1 : 3-diethylbarbituric acid could not be caused to crystallise; the *phenylhydrazone*, $C_{21}H_{22}O_3N_4$, forms long, yellow leaflets, decomp. 164°.

Attempts to cause interaction between barbituric acid and oxalic acid, oxalyl chloride, oxalyl bromide, or phthalic anhydride were not successful. Thiobarbituric acid does not react smoothly with acetic or benzoic anhydrides. The acetyl group of 5-acetylbarbituric acids does not appear to be capable of condensing with aldehydes. H. W.

Alkyl*iso*propylbarbituric Acids. F. Hoffmann La Roche & Co. (Austr. Pat. 92386; from *Chem. Zentr.*, 1923, iv, 665).—In modification of an earlier patent (A., 1922, i, 872) other alkyl halides are used in place of allyl bromide. *5-Methyl-5-isopropylbarbituric acid*, from *iso*propylbarbituric acid and methyl iodide, forms crystals, m. p. 186—187°. *5 : 5-Diisopropylbarbituric acid* forms crystals, m. p. above 230° (decomp.). G. W. R.

Preparation of New Barbituric Acid Compounds. Chemische Fabrik auf Aktien, vorm. E. Schering (Brit. Pat. 198379; addn. to 158558; cf. A., 1922, i, 582).—New compounds,

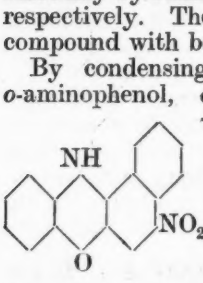
similar in properties to that previously described (*loc. cit.*) are obtained by replacing the diethylbarbituric acid in the original process by dipropyl-, diallyl-, or phenylethyl-barbituric acid. The products of these three fusions melt respectively at 82—86°, 85—88°, and 106—120°. W. T. K. B.

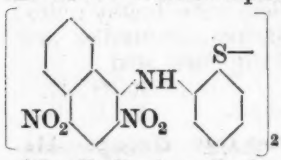
Diketopiperazine Derivatives. P. KARRER, C. GRÄNACHER, and A. SCHLOSSER (*Helv. Chim. Acta*, 1923, **6**, 1108—1112).—Benzyl chloride reacts with the silver salt of glycine anhydride to give 2 : 5-*dihydroxydihydropyrazine dibenzyl ether*, crystallising in white leaflets, m. p. 164°. The reaction therefore follows a different course from that of methyl iodide on the anhydride (A., 1922, i, 235). The new compound is readily hydrolysed by boiling dilute acids to benzyl alcohol and glycine, and in this respect differs markedly from its isomerides, *N* : *N'*-dibenzylglycine anhydride and diketo-2 : 5-dibenzylpiperazine. E. H. R.

New Syntheses in the Quinoneimide Dye Group. I. Syntheses with 1-Chloro-2 : 4-dinitronaphthalene. F. KEHRMANN (with A. VAN BAERLE) (*Ber.*, 1923, **56**, [*B*], 2385—2390).—A number of known and some new quinoneimide dyes have been prepared by condensing 1-chloro-2 : 4-dinitronaphthalene with different bases. In many cases the toluene-*p*-sulphonic ester of Martius's yellow (2 : 4-dinitro-α-naphthol) can also be used.

o-2 : 4-*Dinitronaphthylaminodiphenylamine* is obtained by condensing the dinitrochloronaphthalene with *o*-aminodiphenylamine in alcohol; it forms large, brownish-red prisms containing benzene from that solvent, which lose benzene and turn black at 70°, m. p. 140°. With 5-chloro-2-aminodiphenylamine, the corresponding 5-*chloro*-2-(2 : 4-*dinitronaphthylamino*)*diphenylamine* is obtained, dark brown leaves, m. p. 110°. Both these compounds are reduced smoothly by stannous chloride to rosinduline and chlororosinduline respectively. The rosindones are obtained by fusing the dinitro-compound with benzoic acid.

By condensing 2 : 4-dinitro-1-naphthyltoluenesulphonate with *o*-aminophenol, o-2 : 4-dinitronaphthylaminophenol is obtained which, by careful treatment with aqueous sodium hydroxide is converted into 5-*nitro*-7 : 12-*naphthaphenoxazine* (annexed formula), a violet precipitate which decomposes when heated. An acetyl derivative could not be obtained, but instead the known phenonaphthoxazone was formed. With *oo'*-diaminodiphenyl disulphide the above toluenesulphonate condenses to give o-*bis*-2 : 4-*dinitronaphthylaminophenyl disulphide* (annexed formula), orange-yellow leaflets, m. p. 169°. With *o*-aminothiophenol it gives o-2 : 4-*dinitronaphthylaminophenyl mercaptan*, a lemon-yellow, crystalline powder, m. p. 198°, which by careful treatment with alkali gives 5-*nitro*-7 : 12-*naphthaphenthiazine*, nearly black needles with a brassy reflex, m. p. 156° (decomp). It is much

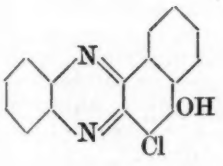




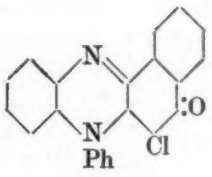
more stable than the corresponding oxazine. A by-product of the last condensation, yellow, glistening crystals, m. p. 150°, appeared to be 2 : 4-*dinitronaphthyl*-o-*aminophenyl sulphide*.

E. H. R.

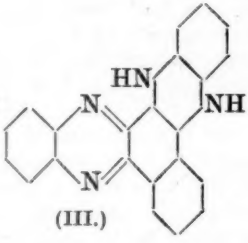
New Syntheses in the Quinoneimide Dye Group. II. Steric Influence in the Condensation of Hydroxyquinones with o-Diamines. F. KEHRMANN [with C. BUFFAT] (*Ber.*, 1923, 56, [*B*], 2390—2394).—It has long been known that substituted quinones such as chloranilic acid and 3-chloro-4-hydroxy-1 : 2-naphthaquinone react with difficulty or not at all with *o*-diamines, but it is now found that these reactions proceed under suitable conditions. Thus when chloranilic acid is heated with *o*-phenylenediamine hydrochloride and a large quantity of benzoic acid at the boiling point, 1 : 4-*dichloro*-2 : 3-*dihydroxyphenazine* is formed, dark brownish-red, metallic crystals, blackening at 310°. It gives a dichroic sulphuric acid solution, brown in thick, greenish-yellow in thin layers. With *o*-aminodiphenylamine, chloranilic acid gives 1 : 4-*dichloro*-2-*hydroxy*a*posafranone*, dark, reddish-brown crystals with a weak, brassy lustre, decomposing at 285°. 3-Chloro-4-hydroxy-1 : 2-naphthaquinone with *o*-phenylenediamine gives 6-*chloro*-5-*hydroxy*-αβ-*naphthaphenazine* (formula I), dark red, brassy crystals decomposing at about 280°. It gives a dirty yellowish-green colour with concentrated sulphuric acid, ponceau-red with hot alkali. With *o*-aminodiphenylamine, 3-chloro-2-hydroxy-1 : 4-naphthaquinone gives 6-*chlororosindone* (formula II), red needles with golden lustre, m. p. 255°, giving a dark yellowish-green colour in sulphuric acid. With 2-amino-5-chlorodiphenylamine, 6 : 9-*dichlororosindone* is formed, red needles with strong gold reflex, m. p. 242—243°, giving a dirty violet-red colour in sulphuric acid.



(I.)



(II.)

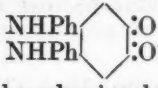


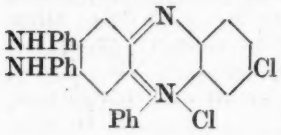
(III.)

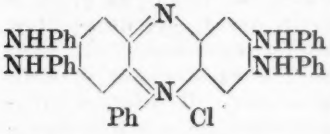
When the above 5-hydroxy-6-chloronaphthaphenazine is fused with *o*-phenylenediamine, a new *dihydronaphthadiphenazine* (formula III) is formed, golden-yellow leaflets with brassy reflex, m. p. 263°. Its *hydrochloride* forms dark red, metallic needles, and it gives a pure green colour in concentrated sulphuric acid.

E. H. R.

New Syntheses in the Quinoneimide Dye Group. III. Syntheses of Induline-3*B* and -6*B*. F. KEHRMANN [with W. KLOPFENSTEIN] (*Ber.*, 1923, **56**, [*B*], 2394—2397).—The con-

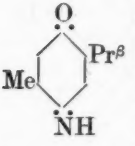
stitutional formulæ assigned to Induline-3*B* and -6*B* have now been confirmed by synthesis of these dyes from dianilino-*o*-quinone,  When this is condensed with 2-amino-5-chlorodiphenylamine hydrochloride in alcohol, 3-*chloro*-8-*anilino-phenyl*a*posafranine* (annexed formula) is formed, crystallising in needles with a green reflex. The free *base* forms brownish-red needles, m. p. 258°. The colour in concentrated sulphuric acid is violet-blue, becoming violet and then Bordeaux-red on dilution. When this is boiled with aniline and aniline hydrochloride, the ring chlorine is replaced by the anilino-group, forming 8-*anilino*-3 : 7-*diphenylphenosafranine*, identical with Induline-3*B*. The free base forms nearly black leaflets with a weak green reflex, m. p. 242°. Induline-3*B* is converted into Induline-6*B*, 2 : 8-dianilino-3 : 7-diphenylphenosafranine (annexed formula), by boiling with aniline and aniline hydrochloride in presence of 1 mol. of mercuric oxide. The free base forms greenish-black metallic crystals, m. p. 286—288°; the *hydrochloride* and *hydrobromide* both form crystals with a coppery lustre, insoluble in water.





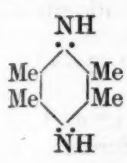
E. H. R.

New Syntheses in the Quinoneimide Dye Group. IV. The Colour of the Simple Quinoneimines. F. KEHRMANN [with B. CORDONE] (*Ber.*, 1923, **56**, [*B*], 2398—2405).—In a previous paper (A., 1922, ii, 333), the rule was established that the effect of salt formation on the colour of basic nitrogen compounds is to intensify the colour if the unsaturated condition persists. This rule has now been found to apply to compounds of the quinoneimine series, of which several new members have been prepared. *Thymoquinonemonoimine* (annexed formula) was prepared by oxidising *p*-aminothymol with silver oxide in ethereal solution; it crystallises in bright yellow, silky leaflets, m. p. 74—75°. It is stable for some time in the dark at low temperatures and is much less sensitive to light than *p*-benzoquinonemonoimine. Its salts are deeper yellow in colour than the compound itself; the *hydrochloride* is obtained as a voluminous, yellow precipitate from ether; the *picrate*, which is stable for some time in water, forms bright yellow, sparingly soluble crystals. The monoimines of benzo- and tolu-quinone were prepared afresh to confirm their yellow colour.

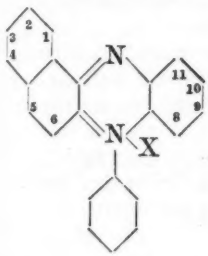


Benzoquinonechloroimine, O: :NCl, is also yellow, but benzoquinonedi-imine is colourless, whilst its dihydrochloride is yellow. Benzoquinonedichlorodi-imine, ClN: :NCl, is colourless; it

gives a salt only with concentrated sulphuric acid, and this is yellow. *Duroquinonedi-imine* (annexed formula) was obtained by oxidising diaminodurene with silver oxide in ether; it forms colourless crystals, not very sensitive to light, m. p. 134—135°. It dissolves in dilute mineral acids, giving bright yellow solutions which soon decompose with deposition of duroquinone. The salts, which can be obtained in crystalline form from ether, are bright yellow. The results show that the carbonyl group is a stronger chromophore than the iminocarbonyl group ·C:NH. This is also shown by the fact that whilst tetramethyldiaminobenzophenone is yellow, auramine base is colourless. E. H. R.

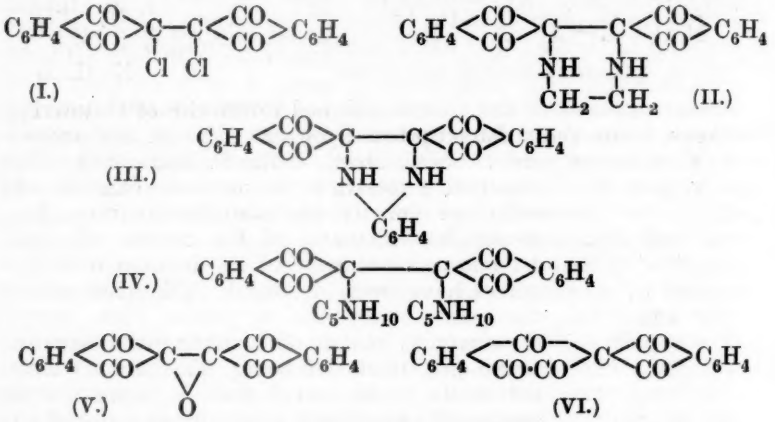


Determination of the Constitutional Formulæ of Colouring Matters from their Absorption Spectra. V. F. KEHRMANN and M. SANDOZ (*Helv. Chim. Acta*, 1923, **6**, 982—994).—The absorption spectra of the mono-acid and di-acid salts of phenyl-αβ-benzophenazonium (annexed formula) and of the mono-, di-, and tri-acid salts of nine of its monoamino-derivatives have been measured. The mono-salt of the parent substance is yellow with orange fluorescence, the di-salt violet; both have an ortho-quinonoid structure. The amino derivatives, 1-, 2-, 3-, and 4- form a group. Their mono-salts are bluish-green, except that of the 3-amino-derivative, which is brown; their di-salts are yellow, similar to the mono-salt of the parent substance, and their tri-salts deep red, comparable with the di-salt of the parent. The 1-amino-compound does not form a tri-salt, probably on account of steric hindrance. All these salts are given an ortho-quinonoid structure. The mono-salt of the 10-amino-derivative (violet) is probably also ortho-quinonoid. The 9- and 5-amino-compounds form another group; they behave similarly to *apo*safranine (A., 1920, ii, 142). The mono-acid salt (scarlet) and the di-acid salt (green) are para-quinonoid, whilst the tri-acid salt (violet) has the ortho-quinonoid structure. The fact that the di-acid salts can be diazotised indicates that the solutions contain a small amount of the yellow, ortho-quinonoid di-acid salt in equilibrium with the para-quinonoid form. Two amino-derivatives, the meta- and para-, were prepared having the amino-group in the external benzene ring. Here the auxochromic effect of the amino-group is reduced to a minimum, and there is little difference between the colours of the mono-acid salt and of the di-acid salt, both being yellow in solution; the tri-acid salt is violet, and all three are ortho-quinonoid. Curves are given showing the absorption spectra of all the salts examined. E. H. R.



Spirans. XII. Heterocyclic Dispirans and the Nature of the Basic Properties of the Imino-group. D. RADULESCU (*Bul. Soc. Ştiinţe Cluj*, 1922, **1**, 356—360; from *Chem. Zentr.*, 1923, iii, 1081; cf. this vol., i, 58).—Heterocyclic dispirans have

been prepared by the author by the action of *o*-diamines on dichlorobisdiketohydrindene (I). *Piperazinebis*-3-1 : 3-*diketohydrindene*-2 : 2 : 3 : 2-*dispiran*, $C_{20}H_{14}O_4N_2$, (II) forms yellow prisms, m. p. 249° (corr.). The *spiran* (III), $C_{24}H_{14}O_4N_2$, forms microcrystalline brown prisms, m. p. 272° (corr.). Spiran III is scarcely basic, whilst the dispiran II is moderately basic. This is explained by Thiele's theory of partial valencies, which is also applicable to the slight basicity of pyrrole and indole. Spirans with tertiary nitrogen



(I.) (II.) (III.) (IV.) (V.) (VI.)

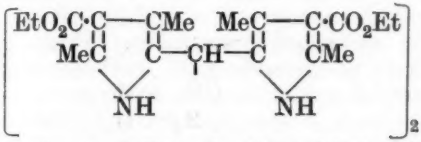
are more basic. N : N′-*Dipiperidylbis*-1 : 3-*diketohydrindene* (IV) forms orange prisms, m. p. 174°. The *diethylamino*-derivative of the latter forms yellow prisms, m. p. 129°, and the *dibenzylamino*-derivative yellow needles, m. p. 178°. The author concludes that the hydroxy-derivatives corresponding with the amines must be strongly acid. The compound described by Gabriel and Leupold (A., 1898, i, 481) as bisdiketohydrindene oxide (V) is really a spiran pinacone (VI). It is hydrolysed by weak acids and alkalis to diketohydrindene, and its decomposition products, and phthalonic acid. G. W. R.

Reactions of certain Substituted Guanidines with Sulphur. G. Bruni and T. G. Levi (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 313—316).—When heated together in a sealed tube at 260—270°, *s*-diphenylguanidine and sulphur give a good yield of mercaptobenzthiazole. In aniline solution, subjected to prolonged boiling in a reflux apparatus, the reaction gives rise to little or no mercaptobenzthiazole, but to anilinobenzthiazole (cf. Hofmann, A., 1880, 388; Jacobson and Frankenbacher, A., 1891, 1048; Hugershoff, A., 1903, i, 865; and Rassow and Döhle, A., 1916, i, 747): $NHPh{\cdot}C(:NH){\cdot}NHPh+S=C_6H_4<\begin{matrix}N\\S\end{matrix}>C{\cdot}NHPh+NH_3$; the *acetyl* derivative of anilinobenzthiazole has m. p. 162—163°.

Mercaptobenzthiazole is formed in good yield when phenylguanidine, and in poor yield when *s*-triphenylguanidine, is heated

in a sealed tube with sulphur at 270° (cf. Sebrell and Bord, this vol., i, 89). T. H. P.

Tetrapyrrlethanes. I. Hans Fischer and M. Schubert (*Ber.*, 1923, **56**, [*B*], 2379—2384; cf. A., 1923, i, 707).—Glyoxal can be condensed with ethyl 2 : 4-dimethylpyrrole-3-carboxylate in alkaline or, better, in acid alcoholic solution, to form *tetra*(3-*carbethoxy*-2 : 4-*dimethyl*-5-*pyrryl*)*ethane* (annexed formula), which crystallises in colourless leaflets, m. p. 282°. It gives an intense green solution in acetic acid. Oxidation with ferric chloride gives 2 mols. of bis-2 : 4-dimethyl-3-carbethoxypyrrylmethene, whilst reduction with hydriodic acid in acetic acid solution gives a mixture of pyrroles containing 2 : 4-dimethyl- and 2 : 4 : 5-trimethyl-pyrrole. Potassium methoxide converts the ethane compound into tetramethylpyrrole. It can also be hydrolysed to *tetra*(3-*carboxy*-2 : 4-*dimethylpyrryl*)*ethane*, small tetrahedral crystals, m. p. 233° (decomp.), but this product is not identical with that obtained by condensing glyoxal with 2 : 4-dimethylpyrrole-3-carboxylic acid.



The relationship of tetrapyrrylethane derivatives with blood- and bile-pigments is discussed, the conclusion being that there is a closer relationship with the latter. This conclusion is supported by spectroscopic examination of copper and zinc salts of a number of dipyrrylmethene derivatives. E. H. R.

Diallylxanthine. Society for Chemical Industry in Basle (Swiss Pat. 97978; from *Chem. Zentr.*, 1923, iv, 830).—By heating 4 : 5-*diamino*-2 : 6-*dioxo*-1 : 3-*diallylpyrimidine*, obtained by condensation of diallylcarbamide with cyanoacetic acid or ethyl cyanoacetate, treatment with nitrous acid, and reduction with formic acid, 5-*formylamino*-4-*amino*-2 : 6-*dioxo*-1 : 3-*diallylpyrimidine* is obtained. This is heated with *N* sodium hydroxide solution at 100° and then acidified, whereby 1 : 3-*diallylxanthine*, m. p. 155—156°, is obtained. The intermediate compound, 4-*amino*-6-*oxo*-5-*oximino*-1 : 3-*diallylpyrimidine*, can also be obtained by direct condensation of *s*-diallylcarbamide with ethyl oximinocyanoacetate. G. W. R.

1 : 3 : 7-Triallylxanthine. Society for Chemical Industry in Basle (Swiss Pat. 97979; from *Chem. Zentr.*, 1923, iv, 830; cf. preceding abstract).—1 : 3-*Diallylxanthine* is alkylated, for example by treatment with allyl benzoate in the presence of ethyl-alcoholic potassium hydroxide at 80°. 1 : 3 : 7-*Triallylxanthine* has m. p. 57—58°; b. p. 176°/5 mm. G. W. R.

Oxidation of Uric Acid with Ferrous Salts. I. M. H. Pfaltz (*J. Amer. Chem. Soc.*, 1923, **45**, 2980—2984; cf. this vol., i, 210).—Cleavage of the uric acid molecule was accomplished by the systems ferrous sulphate–sodium hydrogen carbonate–air and sodium pentacyanoaquoferroate–air or oxygen, but not

by the system ferrous sulphate–oxygen. The action was similar to that which occurred with pyrimidines. F. B.

Action of Alkali on Substituted Uric Acids. I. 9-Phenyl-1 : 3-dimethyluric Acid. E. S. GATEWOOD (*J. Amer. Chem. Soc.*, 1923, **45**, 3056—3064; cf. A., 1923, i, 253).—This substituted uric acid was decomposed instantaneously at 100° with 4*N* sodium hydroxide with the elimination of methylamine. On acidifying the solution, carbon dioxide was evolved, and crystals, m. p. 249—250°, of 3-*phenyl*iso*hydantoin*-5-*carboxyl*-o-*methylamide* separated. This was further decomposed by alkali into phenylcarbamide, methylamine, oxalic acid, and formic acid, whilst oxidation with hydrogen peroxide in alkaline solution yielded 5-*hydroxy*-3-*phenylhydantoin* 5-*carboxyl*-o-*methylamide*, large, thin, rectangular plates, m. p. 195—196°. This was further decomposed by alkali into methylamine, phenylcarbamide, and meso-oxalic acid. 9-*Phenyl*-1 : 7-*dimethyluric acid* was synthesised. It did not melt below 280° and was not affected by boiling with 4*N* sodium hydroxide for ten minutes. F. B.

The Activation of Halogen and Methyl in Aromatic Compounds by the Azo-group, ·N:NR. W. BORSCHE and I. EXSS (*Ber.*, 1923, **56**, [*B*], 2353—2357).—Experiments with 4-chloro-3-nitroazobenzene and 6-chloro-3-nitro-4′-methoxyazobenzene, show that the azo-group in ortho- or para-position to the halogen imparts to it increased activity. These compounds react more readily with hydrazine, ammonia, aniline, or sodium ethoxide than *o*- or *p*-chloronitrobenzene, although not so readily as chloro-2 : 4-dinitrobenzene. On the other hand, benzeneazo-2-nitro-*p*-toluene does not react with benzaldehyde to form a stilbene derivative as does 2 : 4-dinitrotoluene.

4-*Chloro*-3-*nitroazobenzene*, from 4-chloro-3-nitroaniline and nitrosobenzene, forms brown needles, m. p. 84°. 6-*Chloro*-3-*nitro*-4′-*hydroxyazobenzene*, from diazotised 6-chloro-3-nitroaniline and phenol, forms red needles, m. p. 218°; it is methylated by methyl sulphate to 6-*chloro*-3-*nitro*-4′-*methoxyazobenzene*, deep yellow leaflets, m. p. 103°. *Benzeneazo*-2-*nitro*-p-*toluene*, from 2-nitro-*p*-toluidine and nitrosobenzene, forms brown needles, m. p. 106°.

3-*Nitro*-4-*hydrazinoazobenzene*, $Ph{\cdot}N_2{\cdot}C_6H_3(NO_2){\cdot}NH{\cdot}NH_2$, forms red needles, m. p. 206° (decomp.); with acetophenone it forms the corresponding *hydrazone*, $Ph{\cdot}N_2{\cdot}C_6H_3(NO_2){\cdot}NH{\cdot}N{:}CMePh$, red needles, m. p. 195°. 2-*Nitro*-4-*benzeneazo*-4′-*hydroxyazobenzene*, $Ph{\cdot}N_2{\cdot}C_6H_3(NO_2){\cdot}N_2{\cdot}C_6H_4{\cdot}OH$, obtained from the above hydrazine and *p*-benzoquinone, forms brown needles, m. p. 203° (decomp.); with quinoneoxime, the hydrazine forms an *oximehydrazone*, $Ph{\cdot}N_2{\cdot}C_6H_3(NO_2){\cdot}NH{\cdot}N{:}C_6H_4{:}N{\cdot}OH$, a red, crystalline powder, m. p. 235° (decomp.).

3-*Nitro*-4-*aminoazobenzene* forms red needles, m. p. 173·5°. 3-*Nitro*-4-*piperidinoazobenzene*, by condensing 4-chloro-3-nitroazobenzene with piperidine, forms orange-red tablets, m. p. 64°. 3-*Nitro*-4-*anilinoazobenzene*, $Ph{\cdot}N_2{\cdot}C_6H_3(NO_2){\cdot}NHPh$, forms brown needles,

m. p. 124°. 3-*Nitro*-4-*methoxyazobenzene* crystallises in orange-red needles, m. p. 107°.

3-*Nitro*-4′-*methoxy*-6-*hydrazinoazobenzene* forms red needles, m. p. 173°; with *p*-anisaldehyde it gives the corresponding *hydrazone*, red needles, m. p. 208°. 5-*Nitro*-2-*amino*-4′-*methoxyazobenzene* forms brownish-yellow needles, m. p. 136°. 3-*Nitro*-6 : 4′-*dimethoxyazobenzene* forms orange-yellow needles, m. p. 123°. E. H. R.

Thiophenols. V. Salts and Additive Compounds of *oo*′-Azophenyl Methyl Sulphide and *oo*′-Azoxyphenyl Methyl Sulphide. K. Brand and P. Grobel (*Ber.*, 1923, **56**, [*B*], 2563—2567).—An extension of the work of Brand and Wirsing (A., 1912, i, 666; 1913, i, 406) on the para-compounds to the ortho-series.

The following salts of *oo*′-dimethylthiolazobenzene,

$$SMe\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot SMe,$$

are described: the *perchlorate*, $C_{14}H_{14}N_2S_2,HClO_4$, bluish-violet needles which are very sensitive to moisture, m. p. 154°; the *sulphate*, $C_{14}H_{14}N_2S_2,2H_2SO_4$, dark violet needles; the very unstable *hydrochloride*, blue needles, and its additive *compounds* with stannic chloride, $C_{14}H_{14}N_2S_2,HCl,SnCl_4$, blackish-violet needles, with ferric chloride, $C_{14}H_{14}N_2S_2,HCl,FeCl_3$, dark violet, almost black needles, and mercuric chloride, an unstable, blue compound.

oo′-Dimethylthiolazobenzene is transformed by methyl sulphate into the *methosulphate*, $N_2(C_6H_4\cdot SMe_2\cdot O\cdot SO_2\cdot OMe)_2$, coarse crystals, m. p. 189° (decomp.), which is converted into the corresponding *iodide*, $C_{14}H_{14}N_2S_2,2MeI$, long, red needles, m. p. 154°, which readily loses methyl iodide when preserved, the *bromide*,

$$C_{14}H_{14}N_2S_2,2MeBr,$$

m. p. 154°, and the unstable *thiocyanate*, decomp. 102—105°.

o-Nitrophenyl methyl sulphide is reduced by sodium and methyl alcohol to *oo*′-*dimethylthiolazoxybenzene*, crystals, m. p. 72°, from which the corresponding *methosulphate*, $C_{14}H_{14}ON_2S_2,2Me_2SO_4$, yellow leaflets, m. p. (indefinite) 167—169° (decomp.) after becoming red at 160—162°, and the *methiodide*, $C_{14}H_{14}ON_2S_2,2MeI$, m. p. 103° (decomp.), are obtained.

oo′-Dimethylthiolazobenzene and the azoxy-compound combine with iodine in chloroform solution to give the *compounds*,

$$C_{14}H_{14}N_2S_2,2I_2,$$

m. p. 155° after evolving iodine at 140°, and $C_{14}H_{14}ON_2S_2,2I_2$, dark green needles, m. p. 113—114°; the corresponding sulphonium methosulphates when treated in aqueous solution with iodine and potassium iodide yield the *compounds* $C_{14}H_{14}N_2S_2,2MeI,2I_2$, m. p. 113—115° (decomp.), and $C_{14}H_{14}ON_2S_2,2MeI,2I_2$, m. p. 103° (decomp.) after darkening at 100°.

The following additive compounds are described: the *substance*, $C_{14}H_{14}N_2S_2,AgNO_3$, from the components in boiling aqueous-alcoholic solution, orange-coloured needles, which is completely decomposed into its components by hot water; the *salt*,

$$C_{14}H_{14}ON_2S_2,AgNO_3,$$

yellow needles; *oo*′-*diethylthiolazobenzene silver nitrate*,

$$C_{16}H_{18}N_2S_2,AgNO_3,$$

orange-coloured leaflets; *o-nitrophenyl methyl sulphide silver nitrate*, $NO_2 \cdot C_6H_4 \cdot SMe, AgNO_3$, yellow leaflets, m. p. 122°. H. W.

The Influence of Sulphonic Groups on the Colour of Azo-dyes. W. MEULY (*Helv. Chim. Acta*, 1923, **6**, 931—935).—To determine the influence of the number and position of sulphonic groups on the colour of azo-dyes, spectroscopic comparison was made of a large number of secondary bisazo-dyes, in which the first component was an aniline mono- or di-sulphonic or a naphthylamine mono-, di-, or tri-sulphonic acid, the middle component was cresidine (3-amino-*p*-cresol ether) and the end component an α- or β-naphthol mono-, di-, or tri-sulphonic acid. In every case, an additional sulphonic group, in either the first or the end component, deepens the colour, but the effect diminishes as the number of sulphonic groups increases. In the naphtholsulphonic acids, the effect of changing the position of the sulphonic group is smaller than the effect of an additional group. Similar results were obtained with a number of monoazo- and trisazo-dyes. As an example of the effect of additional sulphonic groups, the dye from sulphanilic acid, 3-amino-*p*-cresol ether and 1 : 4-naphtholsulphonic acid is red, whilst the corresponding dye using 1 : 3 : 6 : 8-naphtholtrisulphonic acid is violet. An absorption band may be shifted 10 to 20 $\mu\mu$ by a single sulphonic group, the influence being generally greater in the end component than in the first component. These results apply both to aqueous and to alcoholic solutions; in sulphuric acid and formic acid solutions the absorption bands are shifted in the opposite direction by sulphonic groups. [Cf. *B.*, 86.]

E. H. R.

Certain Double Salts of Diazo-compounds with Lead Tetrachloride. E. SAKELLARIOS (*Ber.*, 1923, **56**, [*B*], 2536—2541).—A series of double salts of the general formula $(ArN_2Cl)_2PbCl_4$ has been prepared. They are generally yellow in colour and insoluble in water. They are decomposed when heated with water with production of phenols. Thermal decomposition in the presence of inert solvents, such as carbon tetrachloride or benzene, gives *p*-chloronitrobenzene from the *p*-nitrodiazonium compound and mixtures of chlorinated benzenes from the benzenediazonium salt. The *p*-tolyl-, *m*-nitrophenyl-, and *p*-chlorophenyl-diazonium compounds are remarkably stable towards heat. The double salts dissolve in concentrated sulphuric acid with separation of lead tetrachloride and production of the diazonium sulphate. They couple immediately with an alkaline solution of β-naphthol and retain this power after being preserved during many months in a desiccator; an exception is, however, provided by the benzenediazonium salt which undergoes rapid decomposition. Direct sunlight and increased temperature facilitate the decomposition in a remarkable degree.

The lead tetrachloride solution is prepared by dissolving lead carbonate in concentrated hydrochloric acid and passing chlorine into the mixture at 10° until the suspended lead chloride is dissolved; excess of chlorine is removed in a current of air. The solution thus

prepared is added to the requisite diazonium solution at −5° when the double salts separate. The following individual substances are described: the salt $(PhN_2Cl)_2PbCl_4$, straw-yellow leaflets, and the similarly constituted *compounds* from *p*-toluidine (a yellow, crystalline powder), *p*-chloroaniline (yellow leaflets), *p*-nitroaniline (yellow leaflets), and *m*-nitroaniline.

Ethylamine hydrochloride and lead tetrachloride give the *compound* $(EtNH_2{\cdot}HCl)_2PbCl_4$, yellow leaflets, which is decomposed by water with formation of ethyldichloroamine, b. p. 89°. H. W.

Characterisation of Aminoazo-derivatives. G. CHARRIER and A. BERETTA (*Gazzetta*, 1923, **53**, 729—760).—The authors find that the reaction suggested by Nietzki and Ernst (A., 1890, 1114) for characterising the primary aromatic amino-group (cf. Reitzenstein, A., 1903, i, 815; Meigen, A., 1908, i, 580; Küchel, *Diss. Giessen*, 1909) and based on the action of 1-chloro-2 : 4-dinitrobenzene in alcoholic solution and in presence of sodium acetate, followed by reduction of the resulting 2 : 4-dinitrodiarylamino-derivative to nitroaminodiarylamino-compound by means of sodium sulphide, is general for all aminoazo-derivatives irrespective of the position of the amino-group to the azo-group. The yield of the condensation product is moderately good from the *p*- and *m*-aminoazo-compounds, but less from the ortho-compounds, especially those of the naphthalene series. However, no resin is formed and the product is usually almost insoluble in alcohol, so that purification is easy.

[With A. NANI, L. ALBANI, A. DE LEONIBUS, G. DRISALDI, P. PAVESI, and O. TAVAZZANI.]—*2′-Benzeneazo-2 : 4-dinitrodiphenylamine*, $NPh{:}N{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_3(NO_2)_2$, obtained by the action of 1-chloro-2 : 4-dinitrobenzene on *o*-aminoazobenzene, forms slender, orange-yellow needles, m. p. 206°, dissolves in concentrated sulphuric acid with a green coloration, and resists boiling acetic anhydride. When suspended in alcohol and treated with sodium sulphide, it yields *2′-benzeneazo-4-nitro-2-aminodiphenylamine*,

$$NPh{:}N{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_3(NH_2){\cdot}NO_2,$$

which crystallises in slender, deep red needles, m. p. 151°, and gives a *benzoyl* derivative, $C_{25}H_{19}O_3N_5$, crystallising in slender, yellow needles, m. p. 199°.

2′-p-Toluneazo-2 : 4-dinitro-4′-methyldiphenylamine,

$$C_6H_4Me{\cdot}N{:}N{\cdot}C_6H_3Me{\cdot}NH{\cdot}C_6H_3(NO_2)_2,$$

prepared from *o*-toluneazo-*p*-toluidine, forms lustrous, red needles, m. p. 232°, gives a green solution in concentrated sulphuric acid, and on reduction with sodium sulphide yields *2′-p-tolueneazo-4-nitro-2-amino-4′-methyldiphenylamine*,

$$C_6H_4Me{\cdot}N{:}N{\cdot}C_6H_3Me{\cdot}NH{\cdot}C_6H_3(NH_2){\cdot}NO_2,$$

which crystallises in reddish-brown needles, m. p. 166°, and gives a *benzoyl* compound, $C_{27}H_{23}O_3N_5$, separating in yellow needles, m. p. 206°.

m-Aminoazobenzene may be obtained in satisfactory yield by benzoylating *m*-nitroaniline, reducing the *m*-nitrobenzanilide to *m*-aminobenzanilide, and converting the latter, by means of nitroso-

benzene, into the benzoyl derivative of *m*-aminoazobenzene. The melting point of *m*-aminoazobenzene, given by Mills (T., 1895, **67**, 917) as 56—57°, is found to be 62°.

3′-*Benzeneazo*-2 : 4-*dinitrodiphenylamine*,

$$NPh{:}N{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_3(NO_2)_2,$$

prepared from *m*-aminoazobenzene, crystallises in orange-yellow leaflets, m. p. 162°, and dissolves in concentrated sulphuric acid, giving a red coloration.

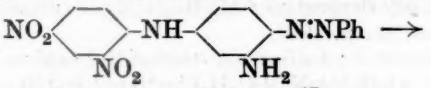
4′-Benzeneazo-2:4-dinitrodiphenylamine, prepared from *p*-aminoazobenzene, has m. p. 176° (cf. Walther and Lehmann, A., 1904, i, 352). 4′-*Benzeneazo*-4-*nitro*-2-*aminodiphenylamine*, $C_{18}H_{15}O_2N_5$, obtained by reducing the preceding compound, forms minute, deep red crystals, m. p. 164°; its *acetyl* compound crystallises in slender, yellow needles, m. p. 153°, and its *benzoyl* derivative in yellow needles, m. p. 226°.

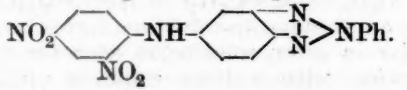
4′-o-*Tolueneazo*-2 : 4-*dinitro*-2′-*methyldiphenylamine*,

$$C_6H_4Me{\cdot}N{:}N{\cdot}C_6H_3Me{\cdot}NH{\cdot}C_6H_3(NO_2)_2,$$

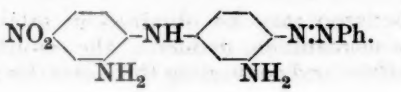
prepared from *o*-tolueneazo-*o*-toluidine, forms deep red needles, m. p. 186°, dissolves in concentrated sulphuric acid to a reddish-violet solution, and, on reduction with sodium sulphide and alcohol, yields 4′-o-*tolueneazo*-4-*nitro*-2-*amino*-2′-*methyldiphenylamine*, which separates in reddish-brown needles, m. p. 159°. 4′-p-*Tolueneazo*-2 : 4-*dinitro*-2′-*methyldiphenylamine*, prepared from *p*-tolueneazo-*o*-toluidine, crystallises in slender, lustrous, red needles, m. p. 151°, and dissolves in concentrated sulphuric acid, giving a violet-red coloration.

The action of 1-chloro-2 : 4-dinitrobenzene on *m*-diaminoazobenzenes results in the replacement by 2 : 4-dinitrophenyl of a hydrogen atom of the amino-group situate in the para-position to the azo-group. The amino-group in the ortho-position to the azo-group does not enter into the reaction, even when the chlorodinitrobenzene is taken in large excess; this appears to be due to the fact that the mono-condensation product is insoluble in alcohol and is hence removed from the sphere of reaction. The resulting diphenylamine derivatives have constitutions analogous to (I) and on oxidation yield the corresponding triazole compounds (II) :

(I.) 

(II.) 

They readily yield monoacetyl and monobenzoyl derivatives, the substituent groups entering the amino-group in the ortho-position to the azo-group. By sodium sulphide in alcoholic solution they are reduced to benzeneazonitrodiaminodiarylamines of the general formula,



4′-*Benzeneazo*-2 : 4-*dinitro*-3′-*aminodiphenylamine*,

$$NPh{:}N{\cdot}C_6H_3(NH_2){\cdot}NH{\cdot}C_6H_3(NO_2)_2,$$

obtained by the action of 1-chloro-2 : 4-dinitrobenzene on 4-benzeneazo-1 : 3-diaminobenzene (chrysoidine), crystallises in bright red needles, m. p. 187°, and gives a violet solution in concentrated sulphuric acid; its *acetyl* compound forms slender, orange-red needles, m. p. 218°, and its *benzoyl* compound, silky, red needles, m. p. 241°. *N*-Phenyl-2′ : 4′-*dinitrophenylamino*(3)*benztriazole* (formula II, above), crystallises in slender, yellow needles, m. p. 188°, and dissolves in concentrated sulphuric acid giving a reddish-yellow coloration.

4′-p-*Chlorobenzeneazo*-2 : 4-*dinitro*-3′-*aminodiphenylamine*,

$$C_6H_4Cl{\cdot}N{:}N{\cdot}C_6H_3(NH_2){\cdot}NH{\cdot}C_6H_3(NO_2)_2,$$

prepared from 4-*p*-chlorobenzeneazo-1 : 3-diaminobenzene, forms lustrous, reddish-brown leaflets, m. p. 220°, and gives a blue solution in concentrated sulphuric acid.

4-p-*Chlorobenzeneazo*-1 : 3-*diaminobenzene* (p-*chlorochrysoidine*), $C_6H_4Cl{\cdot}N{:}N{\cdot}C_6H_3(NH_2)_2$, prepared by the interaction of *p*-chlorophenyldiazonium chloride on *m*-phenylenediamine hydrochloride, crystallises in lustrous, yellow needles, m. p. 140°, and its *hydrochloride* in slender, red needles, m. p. 225°. 4-p-*Bromobenzeneazo*-1 : 3-*diaminobenzene* (p-*bromochrysoidine*), $C_{12}H_{11}N_4Br$, similarly prepared, forms lustrous, golden-yellow needles, m. p. 155°, and its *hydrochloride* red needles, m. p. 213°. 4′-p-*Bromobenzeneazo*-2 : 4-*dinitro*-3′-*aminodiphenylamine*, $C_{18}H_{13}O_4N_6Br$, prepared from the preceding compound, forms lustrous, brick-red needles, m. p. 218°, and dissolves in concentrated sulphuric acid, giving a blue coloration.

4′-*Benzeneazo*-2 : 4-*dinitro*-3′-*amino*-6′-*methyldiphenylamine*,

$$NPh{:}N{\cdot}C_6H_2Me(NH_2){\cdot}NH{\cdot}C_6H_3(NO_2)_2,$$

forms deep red needles, m. p. 273—274°, and dissolves to an emerald-green solution in concentrated sulphuric acid; its *acetyl* derivative forms orange-yellow needles, m. p. 196°, and its *benzoyl* derivative, orange-red needles, m. p. 252°. 4′-*Benzeneazo*-4-*nitro*-2 : 3′-*diamino*-6′-*methyldiphenylamine*, $C_{19}H_{18}O_2N_6$, formed on reduction of the preceding compound by means of sodium sulphide and alcohol, crystallises in lustrous, garnet-red prisms with metallic reflection, m. p. 244°.

4-p-*Chlorobenzeneazo*-1 : 3-*diamino*-6-*methylbenzene* (p-*chloromethylchrysoidine*), $C_6H_4Cl{\cdot}N{:}N{\cdot}C_6H_2Me(NH_2)_2$, prepared from *p*-chlorophenyldiazonium chloride and *m*-tolylenediamine hydrochloride, forms lustrous, golden-yellow leaflets, m. p. 169°, and its *hydrochloride*, lustrous, red needles, m. p. 235°. 4′-p-*Chlorobenzeneazo*-2 : 4-*dinitro*-3′-*amino*-6′-*methyldiphenylamine*,

$$C_{19}H_{15}O_4N_6Cl,$$

prepared from the preceding compound, crystallises in reddish-brown, lustrous needles, m. p. 286°, and dissolves in concentrated sulphuric acid, giving a green coloration; its *acetyl* compound forms slender, orange-yellow needles, m. p. 248°, and its *benzoyl* compound, orange needles, m. p. 285°. On reduction with sodium sulphide in alcoholic solution, it gives 4′-p-*chlorobenzeneazo*-4-*nitro*-

2 : 3′-*diamino*-6′-*methyldiphenylamine*, $C_{19}H_{17}O_2N_6Cl$, which forms slender, reddish-brown crystals, m. p. 262°. 4-p-*Bromobenzeneazo*-1 : 3-*diamino*-6-*methylbenzene* (p-*bromomethylchrysoidine*),

$$C_{13}H_{13}N_4Br,$$

crystallises in lustrous, golden-yellow leaflets, m. p. 177°, and its *hydrochloride* in lustrous, red needles, m. p. 236°. 4′-p-*Bromobenzeneazo*-2 : 4-*dinitro*-3′-*amino*-6′-*methyldiphenylamine*,

$$C_{19}H_{15}O_4N_6Br,$$

prepared from the preceding compound, crystallises in brownish-red leaflets, m. p. 290°, and yields a green solution in sulphuric acid; its *acetyl* derivative forms orange needles, m. p. 242°, and its *benzoyl* derivative, orange-yellow needles, m. p. 275°. 4′-p-*Bromobenzeneazo*-4-*nitro*-2 : 3′-*diamino*-6′-*methyldiphenylamine*,

$$C_{19}H_{17}O_2N_6Br,$$

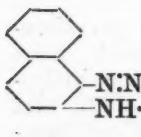
forms reddish-brown leaflets, m. p. 265°.

4-α-*Naphthaleneazo*-1 : 3-*diamino*-6-*methylbenzene*,

$$C_{10}H_7\cdot N{:}N\cdot C_6H_2Me(NH_2)_2,$$

prepared from α-naphthyldiazonium chloride on *m*-tolylenediamine hydrochloride, crystallises in brown needles with green, metallic reflection, m. p. 148°. 4′-α-*Naphthaleneazo*-2 : 4-*dinitro*-3′-*amino*-6′-*methyldiphenylamine*, $C_{10}H_7\cdot N{:}N\cdot C_6H_2Me(NH_2)\cdot NH\cdot C_6H_3(NO_2)_2$, obtained from the preceding compound, forms reddish-brown needles with violet metallic reflection, m. p. 286°; its *acetyl* compound forms red needles, m. p. 268°, and its *benzoyl* compound, yellow needles, m. p. 246°. 4′-α-*Naphthaleneazo*-4-*nitro*-2 : 3′-*diamino*-6′-*methyldiphenylamine*, $C_{23}H_{20}O_2N_6$, forms reddish-brown needles, m. p. 214°. 4-β-*Naphthaleneazo*-1 : 3-*diamino*-6-*methylbenzene* (β-*naphthylmethylchrysoidine*), $C_{17}H_{16}N_4$, crystallises in yellow needles, m. p. 242°. 4-β-*Naphthaleneazo*-2 : 4-*dinitro*-3′-*amino*-6′-*methyldiphenylamine* forms a reddish-brown, crystalline powder, chars, without melting, above 300°, and gives a green solution in concentrated sulphuric acid; its *acetyl* compound separates in slender, yellow needles, m. p. 272°, and its *benzoyl* compound in orange needles, m. p. 267°. 4-β-*Naphthaleneazo*-4-*nitro*-2 : 3′-*diamino*-6′-*methyldiphenylamine*, $C_{23}H_{20}O_2N_6$, forms minute, reddish-brown crystals, m. p. 261°.

α - *Benzeneazo* - β - *naphthyl* - 2 : 4 - *dinitrophenylamine* (annexed formula), prepared by the action of 1-chloro-2 : 4-dinitrobenzene on α-benzeneazo-β-naphthylamine, crystallises in slender, red needles, m. p. 285°, and gives a greenish-blue solution in concentrated sulphuric acid. α-*Benzeneazo*-β-*naphthyl*-4-*nitro*-2-*aminophenylamine*, $NPh{:}N\cdot C_{10}H_6\cdot NH\cdot C_6H_3(NH_2)\cdot NO_2$, forms reddish-brown needles, m. p. 147°.



α-o-*Tolueneazo*-β-*naphthyl*-2 : 4-*dinitrophenylamine*, $C_{23}H_{17}O_4N_5$, obtained from α-*o*-tolueneazo-β-naphthylamine, crystallises in slender, red needles, m. p. 223°, and dissolves in concentrated sulphuric acid to a greenish-blue solution. α-m-*Tolueneazo*-β-*naphthylamine* has m. p. 103—104°. α-m-*Tolueneazo*-β-*naphthyl*-2 : 4-*dinitrophenylamine* forms slender, red needles, m. p. 245°,

and gives a greenish-blue solution in concentrated sulphuric acid. α-m-*Tolueneazo*-β-*naphthyl*-4-*nitro*-2-*aminophenylamine*, $C_{23}H_{19}O_2N_5$, is obtained as a dark red, microcrystalline powder, m. p. 116°. α-p-*Tolueneazo*-β-*naphthyl*-2 : 4-*dinitrodiphenylamine* crystallises in slender, red needles, m. p. 280°, and dissolves in concentrated sulphuric acid to a green solution. α-p-*Tolueneazo*-β-*naphthyl*-4-*nitro*-2-*aminophenylamine* forms microscopic, reddish-brown crystals, m. p. 155°.

α-p-*Chlorobenzeneazo*-β-*naphthyl*-2 : 4-*dinitrophenylamine*, $C_{22}H_{14}O_4N_5Cl$, crystallises in slender, bright red needles, m. p. 278°, and dissolves in concentrated sulphuric acid to a deep blue solution. α-p-*Bromobenzeneazo*-β-*naphthylamine*, $C_6H_4Br{\cdot}N{:}N{\cdot}C_{10}H_6{\cdot}NH_2$, forms red crystals, m. p. 135—136°. α-p-*Bromobenzeneazo*-β-*naphthyl*-2 : 4-*dinitrophenylamine* crystallises in slender, red needles, m. p. 263°, and gives a deep blue solution in concentrated sulphuric acid. 4-*Benzeneazo*-α-*naphthyl*-2 : 4-*dinitrophenylamine*, obtained from 4-benzeneazo-α-naphthylamine, forms long, bright-red, silky needles, m. p. 200°, and colours concentrated sulphuric acid bright blue. 4-*Benzeneazo*-α-*naphthyl*-4-*nitro*-2-*aminophenylamine* separates in minute, reddish-brown crystals, m. p. 181°, and its *acetyl* compound slender, red needles, m. p. 216°.

4-o-*Tolueneazo*-α-*naphthyl*-2 : 4-*dinitrophenylamine*, $C_6H_4Me{\cdot}N{:}N{\cdot}C_{10}H_6{\cdot}NH{\cdot}C_6H_3(NO_2)_2$, forms lustrous, reddish-brown crystals, m. p. 224°, and dissolves in concentrated sulphuric acid to a deep blue solution. 4-p-*Tolueneazo*-α-*naphthyl*-2 : 4-*dinitrophenylamine* crystallises in lustrous, bright red needles, m. p. 207°, and gives a blue solution in concentrated sulphuric acid. 4-p-*Tolueneazo*-α-*naphthyl*-4-*nitro*-2-*aminophenylamine* separates in reddish-brown crystals, m. p. 200°.

4-o-*Nitrobenzeneazo*-α-*naphthylamine*, $NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_{10}H_6{\cdot}NH_2$, crystallises in slender, metallic green needles, m. p. 165°. 4-o-*Nitrobenzeneazo*-α-*naphthyl*-2 : 4-*dinitrophenylamine*, $NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_{10}H_6{\cdot}NH{\cdot}C_6H_3(NO_2)_2$, forms a reddish-brown, microcrystalline powder, m. p. 212°, and yields a blue solution in concentrated sulphuric acid. 4-p-*Nitrobenzeneazo*-α-*naphthylamine* crystallises in deep red needles with metallic reflection, m. p. 252°. 4-p-*Nitrobenzeneazo*-α-*naphthyl*-2 : 4-*dinitrophenylamine* separates in slender, brownish-red needles, m. p. 263°, and dissolves in concentrated sulphuric acid giving a violet coloration.

4-p-*Chlorobenzeneazo*-α-*naphthyl*-2 : 4-*dinitrophenylamine*, $C_{22}H_{14}O_4N_5Cl$, forms slender, orange needles, m. p. 258°, and gives a green solution in concentrated sulphuric acid. 4-p-*Chlorobenzeneazo*-α-*naphthyl*-4-*nitro*-2-*aminophenylamine* separates in slender, deep red crystals, m. p. 228°.

4-α-*Naphthaleneazo*-α-*naphthyl*-2 : 4-*dinitrophenylamine*, $C_{10}H_7{\cdot}N{:}N{\cdot}C_{10}H_6{\cdot}NH{\cdot}C_6H_3(NO_2)_2$, crystallises in slender, brownish-red needles, m. p. 203°, and dis-

solves to a blue solution in concentrated sulphuric acid. 4-β-*Naphthaleneazo-α-naphthyl-2* : 4-*dinitrophenylamine* forms reddish-brown needles, m. p. 241°, and dissolves in concentrated sulphuric acid giving a blue solution. T. H. P.

Reduction of Semicarbazones. E. J. Poth and J. R. Bailey (*J. Amer. Chem. Soc.*, 1923, **45**, 3001—3008; cf. A., 1922, i, 880).—Semicarbazones were reduced to the corresponding semicarbazides under a pressure of $1\frac{2}{3}$—$2\frac{1}{3}$ atm. of hydrogen in the presence of colloidal platinum. The minimum proportion of platinum necessary for efficient reaction varied considerably and when the reduction produced a basic substance the yield was increased by the addition of acid; the amount of acid required varied greatly. The following semicarbazides were prepared. *Fenchylsemicarbazide*, short needles, m. p. 181°. *Benzoylfenchylsemicarbazide*, a crystalline powder, decomp. 226°. *α-Phenylcarbamylfenchylsemicarbazide*, thin plates, m. p. 192°. *Carvomenthylsemicarbazide*, thin plates, m. p. 126° (decomp.), and its *hydrochloride*, short needles, decomp. 186°. *Benzoylcarvomenthylsemicarbazide*, m. p. 235°. *α-Phenylcarbamylcarvomenthylsemicarbazide*, clusters of radiating needles, m. p. 205°. cyclo*Hexylsemicarbazide*, needles, decomp. 185°, and its *hydrochloride*, m. p. 176—178°. *Benzoyl*cyclo*hexylsemicarbazide*, fine needles, m. p. 267° (decomp.). *α-Phenylcarbamyl*cyclo*hexylsemicarbazide*, microscopic short needles, decomp. 236°. Benzylsemicarbazide. *Benzoylmenthylsemicarbazide*, a crystalline powder, m. p. 216° (decomp.). *α-Phenylcarbamylmenthylsemicarbazide*, radiating needles, decomp. 184°. In the preparation of *iso*propyl, bornyl, and menthyl semicarbazides the proportion of colloidal platinum may be considerably reduced with advantage. The following triazoles were obtained by boiling the corresponding acyl semicarbazide with caustic alkali. 3-*Hydroxy-5-phenyl-1-fenchyltriazole*, thick, triangular plates, m. p. 234°. 3-*Hydroxy-5-phenyl-1-carvomenthyltriazole*, thin plates, m. p. 187°. 3-*Hydroxy*-1-cyclo*hexyl-5-phenyltriazole*, slender prisms, m. p. 232—234°. F. B.

Behaviour of Semicarbazides at Elevated Temperatures. E. J. Poth and J. R. Bailey (*J. Amer. Chem. Soc.*, 1923, **45**, 3008—3012; cf. preceding abstract).—cyclo*Hexylsemicarbazide*, when heated at 200° during twelve minutes yielded *di*cyclo*hexylcarbazide* (I), $CO(NH{\cdot}NH{\cdot}C_6H_{11})_2$, plates, m. p. 187°, and unchanged semicarbazide. When the semicarbazide was heated for one and a half hours at 180—185° the products were cyclo*hexylurazole* (II) $\begin{matrix}NH\text{–}CO\\ \\ CO{\cdot}NH\end{matrix}\!\!>\!N{\cdot}C_6H_{11}$, thin, prismatic plates, m. p. 271°, and *di*cyclo*hexylurazine* (III), $C_6H_{11}{\cdot}N\!<\!\begin{matrix}NH{\cdot}CO\\ \\ CO{\cdot}NH\end{matrix}\!\!>\!N{\cdot}C_6H_{11}$, needles or prisms, m. p. 197°; (I) was obtained in good yield when the semicarbazide was mixed with half its weight of urethane and heated at 160°, (II) was prepared by heating the semicarbazide and carbamide in molecular proportions, and (III) by decomposing the hydrochloride of the corresponding semicarbazide. F. B.

Arylazides. I. Conversion of *p*-Methylarylazides into Homologues of Quinol in Presence and Absence of Phenol. E. BAMBERGER and J. BRUN (*Helv. Chim. Acta*, 1923, **6**, 935—941).—Some further experiments on the conversion of arylazides into homologues of quinol (cf. A., 1921, i, 716) are described. *p*-Tolylazide (5 g.) boiled with dilute sulphuric acid (1 : 3 by volume) gives about 1 g. of toluquinol, with some *p*-toluidine, a strong odour of cresol, but no aminocresol. From 25 g. of *m*-4-xylylazide, boiled for nine hours with dilute sulphuric acid, there were obtained 1·8 g. 1 : 3-dimethylquinol, 0·2 g. *as-m*-xylenol, 4·2 g. *as-m*-xylidine, and a considerable quantity of amorphous acids, bases, and resin. When *p*-tolylazide was boiled as before in dilute acid in presence of excess of phenol, from 6 g. of azide, 4·27 g. of *p*-hydroxyphenyl-*p*-tolylamine was obtained, and about 0·32 g. of toluquinol. The theory of the reactions involved has been previously discussed (*loc. cit.*).

E. H. R.

Arylazides. II. The Conversion of *p*-Methylarylazides into Imino-ψ-quinols and ψ-Quinols. E. BAMBERGER and J. BRUN (*Helv. Chim. Acta*, 1923, **6**, 942—951).—Practical details are given of experiments previously reported (A., 1921, i, 716).

E. H. R.

Partial Decomposition of Proteins. E. ABDERHALDEN (*Z. physiol. Chem.*, 1923, **131**, 284—295).—A general description is given of the method of isolating the products of the partial hydrolysis of proteins. The protein is treated with 70% sulphuric acid at a low temperature, *e.g.*, at the ordinary temperature, or at blood heat, and the course of hydrolysis is followed by estimating the amino-nitrogen and comparing it with the total nitrogen, of which an estimation is made on the original protein. The sulphuric acid is removed as barium sulphate, and the filtrate is concentrated in a vacuum. If the product is a solid, it is extracted directly with ether in a Soxhlet apparatus; if it is a syrup, it is mixed with sand to a thick consistency and then extracted. It is afterwards extracted in turn with ethyl acetate, acetone, or methyl alcohol, and if necessary with other solvents such as chloroform or butyl alcohol. It is usually possible after evaporation of the solvent to obtain the fractions in a crystalline form, and they are purified according to their particular composition. In particular cases, variations at any stage may be advisable.

In an attempt to obtain the maximum yield of *d*-alanylglycine anhydride from silk clippings, the residue after hydrolysis, removal of sulphuric acid, and concentration, was treated with alcohol and hydrogen chloride, evaporated to dryness, and the residue dissolved in alcohol. The ammonium chloride separating at once on saturation with ammonia was filtered off. On keeping at 37°, a series of crystalline fractions was obtained, which were extracted in a Soxhlet apparatus with ethyl acetate. Eighty-five g. of pure glycylalanine anhydride was obtained from 1 kg. of silk clippings. Small quantities of glycyl-*l*-tyrosine anhydride and of *d*-alanyl anhydride (dimethylpiperazine) were also obtained.

One kg. of casein was hydrolysed with 10% sulphuric acid at 80°, and the product extracted with ethyl acetate, when 2·5 g. of crystals were obtained, decomp. 280°, and this compound proved to be *l*-leucyl-*d*-valine anhydride. On extracting the residue from the ethyl acetate extraction with acetone, crystals were obtained which on hydrolysis yielded leucine, valine, and glutamic acid, but there was no guarantee that the compound was pure. On further extraction with methyl alcohol, *d*-alanyl-*l*-leucine was obtained along with a crystalline *compound*, $C_{14}H_{23}O_3N_3$, m. p. 192°, $[\alpha]$ −183°, which yielded proline, *l*-leucine, and *d*-alanine on hydrolysis. It is apparently an anhydride formed from these acids by the elimination of 3 mols. of water. W. O. K.

The Formation of Carbon Dioxide during the Breakdown of Proteins in the Autoclave. V. S. SADIKOV (*Biochem. Z.*, 1923, **143**, 492—495).—The method used for the catalytic hydrolysis of proteins by dilute hydrochloric acid under pressure (A., 1923, i, 867) leads in the case of gelatin to a slight formation of carbon dioxide amounting to 2% of the protein. It is suggested that this arises by decarboxylation of the amino-acids under the conditions used. Increasing pressure favours carbon dioxide formation. Nitrogen is also present in the residual gas in the autoclave and oxygen is largely absorbed during the process. J. P.

Hydrolysis in an Autoclave containing Nitrogen. V. S. SADIKOV (*Biochem. Z.*, 1923, **143**, 496—503).—Arising from the author's work on the catalytic hydrolysis of proteins under pressure (cf. preceding abstract), it is found that a retention of nitrogen results when this is carried out in an atmosphere of the gas. Dextrose gives negative results, but a fixation is observed in the case of aspartic acid and to a less extent in the case of glycine. Similar treatment of fumaric and succinic acids in the autoclave leads to a notable retention of nitrogen, which is ascribed to the unsaturated compounds arising from these acids. J. P.

Separation of Proteins of White of Egg by the Acetone Method. M. PIETTRE (*Compt. rend.*, 1924, **178**, 91—93).—Details are given for the separation of the proteins of white of egg into a globulin, ovalbumin (coagulating at 52·5—53°, and having α_D −41·25°), and a glucoprotein. The latter (α_D −62·47°) reduces boiling Fehling's solution, and, at a moderate temperature, mercury and bismuth salts (in presence of alkali) and ammoniacal silver nitrate. E. E. T.

A Further Method of Determining the Isoelectric Point of Proteins and its Application to the Serum-albumins of Various Animals. L. MICHAELIS and T. NAKASHIMA (*Biochem. Z.*, 1923, **143**, 484—491).—The optimum precipitation point of a mixture of mastic and gelatin in the presence of an acetate buffer approaches the isoelectric point of the latter as its relative amount is increased. This observation is made the basis of a method of determining the isoelectric points of various serum-albumins. To a series of tubes containing mastic sol and an acetate buffer at

varying known p_H, increasing amounts of the albumin are added, and the p_H of the zone of optimum precipitation is observed to rise to a constant value beyond which addition of the albumin produces no further shift. This maximum p_H corresponds with the isoelectric point. The following values for the albumins examined were found: ox and guinea-pig, 4·65; dog, 4·66; puppy, 4·67; turtle and man, 4·68. J. P.

Nature of the Reaction between Carbophosphide and Blood-serum. G. CUNEO (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 294—298; cf. this vol., i, 100).—The interaction of carbophosphide and blood-serum yields a phospho-albumin which contains phosphorus in organic combination and either in the most highly oxidised state or as metaphosphoric acid. Since, further, nuclein bases occur among its products of hydrolysis, this phospho-albumin probably owes its existence to a hydrolytic process coupled with atmospheric oxidation, as a result of which the phosphorus of the carbophosphide enters the protein molecule as phosphoric oxide or as a hydrate of the latter. T. H. P.

Nature of the Reaction between Carbophosphide and Blood-serum. G. CUNEO (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 353—357; cf. this vol., i, 100, and preceding abstract).—The author has now investigated the behaviour of blood-serum towards a number of different compounds, some free from, and others containing phosphorus. Certain of these compounds do not denature the serum albumin molecule, which remains phosphorus-free, normally digestible by gastric juice, and without hindering effect on putrefactive processes. On the other hand, phosphorus di-iodide, ethylphosphine, and sodium hypochlorite effect denaturation of the protein molecule, the reaction, like that produced by carbophosphide, being probably of the nature of an auto-oxidation. The reaction of the serum-albumin with hypochlorite is complex, but the principal product is devoid of iron and phosphorus and exhibits the chemical and biological properties of the nucleic acids. T. H. P.

Formation of Methæmoglobin. II. W. HEUBNER and H. RHODE. **III.** R. MEIER. **IV.** W. HEUBNER and R. MEIER. **V.** W. HEUBNER, R. MEIER, and H. RHODE (*Arch. expt. Path. Pharm.*, 1923, **100**, 117—127, 128—136, 137—148, 149—161).—I. A comparison of various substances which convert oxyhæmoglobin into methæmoglobin shows that the actions of potassium ferricyanide and of *p*-benzoquinone are almost identical in this respect.

Although the compound of hæmoglobin with nitric oxide is resistant to the action of reducing agents, it may be decomposed by means of indifferent gases and also by dialysis.

II. Optical and gasometric observations show that by the use of ferricyanide or of *p*-benzoquinone in varying proportions it is possible to produce a mixture of oxyhæmoglobin and methæmoglobin with the two constituents in any desired proportions. The

last traces of oxyhæmoglobin are converted into methæmoglobin more easily by ferricyanide than by *p*-benzoquinone.

III. In the presence of hæmoglobin, quinol, *p*-aminophenol and hydrazobenzene are rapidly oxidised by atmospheric oxygen. Whereas the oxidation products of the first two of these substances are active in forming methæmoglobin, that of hydrazobenzene is not; the formation of methæmoglobin by hydrazobenzene therefore, must be due to an activation of the atmospheric oxygen in the process of oxidation of this substance.

Nitrosobenzene converts oxyhæmoglobin in part into methæmoglobin and in part into reduced hæmoglobin.

IV. Phenylhydroxylamine converts oxyhæmoglobin into methæmoglobin and is itself simultaneously converted into azoxybenzene; excess of phenylhydroxylamine in this reaction reduces the methæmoglobin first formed to hæmoglobin. Reduced hæmoglobin is unaltered optically by phenylhydroxylamine.

m-Nitrophenylhydroxylamine reacts similarly to phenylhydroxylamine but not so strongly. C. R. H.

The Natural Porphyrins. IV. Ooporphyrin. HANS FISCHER and F. KÖGL (*Z. physiol. Chem.*, 1923, **131**, 241—261).—Three hundred g. of gull's egg-shells were extracted with methyl alcohol containing hydrogen chloride, the extract was concentrated, made alkaline with sodium carbonate, and the precipitate washed and dried at 100°. The material was extracted with chloroform, which was then distilled off, and the residue dissolved in a little chloroform, precipitated by the addition of light petroleum, collected on a filter, and dried. It was then again dissolved in a little chloroform, and boiling methyl alcohol was added. *Ooporphyrin dimethyl* ester, $C_{34}H_{36}O_2N_4(OMe)_2$, was obtained as leaflets grouped in rosettes, m. p. 225—230°. The absorption bands of this compound are described at length. They resemble those of Kammerer's porphyrin. When ooporphyrin methyl ester from the shell of the gull or of the plover egg is treated with powdered iron in boiling acetic acid, crystals are obtained which although similar, are not identical, crystallographically and spectroscopically. The absorption bands of solutions of ooporphyrin from the egg-shells of various species of birds are described. W. O. K.

The Precipitation of the Lactoproteins by Copper Salts. A. J. J. VANDEVELDE (*Bull. Soc. chim. Belg.*, 1923, **32**, 376—386).—The lactoproteins have been precipitated by the addition of various salts of copper (sulphate, chloride, nitrate, and acetate) and the effect of washing the precipitates by water has been examined. With the sulphate, chloride, and nitrate, the results obtained are practically identical. Apart from the case of the acetate precipitate, washing by water appears to have no influence on the composition of the precipitate and its copper content. A second series of experiments was carried out to determine the composition of the solid and liquid phases forming the primitive complex. The results obtained show that the quantity of copper in the precipitates increases as the initial concentration of the copper increases,

whilst the ratio of the quantity of copper precipitated to the total quantity of copper employed diminishes, generally in proportion as the initial concentration of the copper increases. The anion present is shown to have a visibly marked effect on the precipitation of the metallic kation. Galeotti's conclusions (A., 1904, i, 355) as to the equilibrium between the proteins and sulphate of copper are not upheld. F. G. P.

Triphosphonucleic Acid and Thymic Acid. S. J. THANNHAUSER (*Z. physiol. Chem.*, 1923, **131**, 296—303; cf. Feulgen and Rosenbeck, A., 1923, i, 618, and Feulgen, *ibid.*, i, 964; also Thannhauser and Sachs, A., 1920, i, 201).—The author has found that after hydrolysing triphosphonucleic acid by alkali, the adenosine may be precipitated as picrate and has obtained almost the theoretical yield of this picrate. He does not admit the validity of the criticism of Feulgen (*loc. cit.*), who doubts the existence of the acid, but he considers that triphosphonucleic acid is with great probability a pure substance. The author also criticises the results of Feulgen (cf. *loc. cit.*) regarding thymic acid. W. O. K.

Influence of Time on the Physico-chemical Properties of Gelatin Solutions. R. DE IZAGUIRRE (*Kolloid Z.*, 1923, **33**, 337—347).—The effect of time on the viscosity, multi-rotation, and the action of electrolytes on gelatin solutions has been examined. It is shown that in the presence of hydrochloric acid the influence of time on the viscosity of gelatin solutions passes through a minimum with increasing concentration of hydrochloric acid. This minimum corresponds with the initial viscosity of the solution. The same regularity is found with the time change of the osmotic pressure, whereby the change with time is smaller the larger the osmotic pressure. Since the maximum of the viscosity and the osmotic pressure is closely connected with the swelling, it follows that the time change takes place in the opposite sense to the swelling, that is, the greater the degree of swelling the smaller the time change. Since the viscosity serves as a measure of the gelatinisation this must be regarded as an " unmixing " process and not as the formation of a hypothetical new modification of the gelatin. The optical rotation of gelatin solutions increases with time in such a way that a curve plotted between the logarithm of the angle of rotation and the logarithm of the time is a straight line. The multirotation is expressed by the formula $[\alpha]_D = K.t^n$, in which for a 1% solution of gelatin $K=209$ and $n=0{\cdot}082$. J. F. S.

The Isoelectric Point of Gelatin from Hide and Bone. O. GERNGROSS and S. BACH (*Biochem. Z.*, 1923, **143**, 542—552).—The isoelectric points of various preparations of gelatin have been found to range from p_H 4·45 to 5·55 according to their source. [Cf. also *B.* Feb.] J. P.

The Displacement of the Isoelectric Point of Gelatin by Formaldehyde. O. GERNGROSS and S. BACH (*Biochem. Z.*, 1923, **143**, 533—542).—The isoelectric points of two preparations of

gelatin were lowered from p_H 5·05 to 4·6 and from p_H 4·75 to 4·3, respectively, by the presence of formaldehyde. J. P.

Points of Minimum Swelling of Ash-free Gelatin. J. A. WILSON and E. J. KERN (*J. Amer. Chem. Soc.*, 1923, **45**, 3139—3140; cf. A., 1923, i, 68).—The two points of minimum in the curve showing the degree of swelling of gelatin as a function of the p_H value, namely at 4·7 and 7·7, were confirmed when using ash free gelatin. The points coincide with those at which minimum values for the wave-length of maximum absorption in the ultra-violet are observed. F. B.

Diffusion of Arsenic [Trioxide] in Gelatin. R. SCHAEFER (*Kolloid Z.*, 1923, **33**, 286—289).—A clear, transparent gel containing arsenious oxide and suitable for dental purposes, may be prepared by adding a few c.c. of hot 30% gelatin solution to a hot solution of arsenious oxide with vigorous stirring. The solution is evaporated slowly on a water-bath and every fifteen minutes a quarter of the evaporated water is replaced by gelatin solution. This process is continued until the concentration desired is reached and the whole allowed to cool to a clear gel. In this way, a gel containing 12—15% of arsenious oxide and 20—30% of gelatin is obtained. The diffusion of arsenious oxide in gelatin has been investigated by laying small portions of the above described gel, and a paste of the powdered oxide and water on a large piece of gelatin and, after sufficient time has elapsed, examining the gelatin by exposing it to hydrogen sulphide. In the case of the arsenic gel, it is found that the amount of arsenic diffused falls off quite regularly as the distance travelled increases, but with the paste there is no apparent diffusion beyond the surface of the gelatin, although this has undoubtedly taken place. The author is of the opinion that in the paste simple molecules are present, but in the gel more complicated molecules are present and these move more slowly, but the total amount of arsenic diffused is greater in the latter case than in the former. J. F. S.

Reaction of Alkaloids with Gelatin [Solutions] containing Iodine. H. HANDOVSKY and E. DU BOIS-REYMOND (*Kolloid Z.*, 1923, **33**, 347—348).—Liesegang rings are produced when a solution of 1 : 1000 pilocarpine hydrochloride is placed on a gel containing 3% of gelatin, 0·6% of potassium iodide, and 0·4% of iodine. The rings are alternately reddish-yellow and dark brown, and are about 1—2 mm. apart. Similar, but differently coloured, rings are produced with strychnine nitrate 1 : 1000 and papaverine hydrochloride 1 : 100. J. F. S.

The Composition of Spinning Silk. E. ABDERHALDEN (*Z. physiol. Chem.*, 1923, **131**, 281—283).—From the product of the hydrolysis of spinning silk by 70% sulphuric acid at 37° there has been isolated glycyl-*l*-tyrosine anhydride, m. p. 282°, and glycyl-*d*-alanine anhydride, m. p. 245°. W. O. K.

The Influence of Temperature on the Action of Amylase. The Action on the Saccharifying Power of Amylase. T. CHRZĄSZCZ (*Biochem. Z.*, 1923, **142**, 417—439).—The influence of temperature on the activity of the amylases of various cereals at the optimum p_H of 4·9 is not uniform. The optimum ranges found are: for barley amylase 49—54°, for rye and wheat amylases 49—55°, for oats amylase 51—53°, and for buckwheat amylase 50—55°. In the cases of maize (56—57°) millet (58—59°), and African millet (62—64°) the optima quoted in brackets lie above the temperatures at which destruction of the enzyme begins. In aqueous solutions, barley amylase is inactivated at 61—62°, rye and wheat amylases at 63—64°, and the other varieties at 65—66°. In general, plant amylases are completely destroyed in one hour when exposed to a temperature of 75°. Amylases from the same genera but of different varieties show the same susceptibility to alteration of temperature at the optimum p_H. Aqueous malt extracts prepared by shaking for at least one hour give a precipitate when heated at 50°, but if the shaking be of shorter duration (thirty minutes), precipitation does not commence below 55—60°. The precipitate does not affect the activity of the enzyme. Rye-malt extract is exceptional in giving at most a slight opalescence even at 80°. J. P.

Potato Amylase. H. HAEHN and H. SCHWEIGART (*Biochem. Z.*, 1923, **143**, 516—526).—Potato amylase is activated by sodium chloride and fluoride, and by potassium, calcium, barium, and magnesium chlorides. It is inhibited by the salts of the heavy metals. Amino-acids have an activating effect (cf. Doby, *Biochem. Z.*, 1914, **67**, 166). Potato amylase after being freed from most of its salts by dialysis or ultra-filtration loses much, but not all, of its activity, but is reactivated by the addition of the salts of the alkali or alkaline-earth metals. A method of combined dialysis and ultra-filtration yields inactive, salt-free preparations of the amylase, which are reactivated by salts. It is concluded that potato amylase consists of an inactive organic constituent together with an indispensable activating mineral salt. J. P.

The Hexose Monophosphatase of Takadiastase. J. NOGUCHI (*Biochem. Z.*, 1923, **143**, 190—194).—A phosphatase is present in takadiastase which hydrolyses barium and sodium hexose monophosphates at 37°. In the former case, barium phosphate separates as a gel, and in the latter the extent of the hydrolysis, which may be practically quantitative, is dependent on the concentration of the enzyme. J. P.

The Cellase of Takadiastase. C. NEUBERG and O. ROSENTHAL (*Biochem. Z.*, 1923, **143**, 399—401).—Takadiastase contains a cellase which at 37° completely hydrolyses cellobiose to dextrose in five days. J. P.

Hemicellusose. IV. Cellobiase and Lichenase. H. PRINGSHEIM and J. LEIBOWITZ (*Z. physiol. Chem.*, 1923, **131**, 262—268).—Lichenin, which is hydrolysed to dextrose by malt extract, has

been acetylated and then hydrolysed to octoacetylcellobiose (Karrer and Joos, A., 1923, i, 541). It ought therefore to be possible to show that malt extract hydrolyses it first to cellobiose by means of a lichenase, and then to glucose by cellobiase, *i.e.*, to show that both lichenase and cellobiase are present in malt extract. This is verified as cellobiose is hydrolysed to dextrose by malt extract at 37°, and p_H 5, and on the other hand, malt extract, after being kept for three months, hydrolyses lichenin only to cellobiose, as the cellobiase apparently disappears on keeping. The presence of cellobiose was determined by the determination of the reducing power and of the rotation of the solution, and also by the formation of the osazone. W. O. K.

Synthetic Action of α-*d*-Mannosidase in Presence of some Monohydric Alcohols. H. Hérissey and J. Cheymol (*Compt. rend.*, 1924, **178**, 123—125).—α-*d*-Mannosidase effects a partial conversion of mannose, in presence of ethyl, propyl, *iso*propyl, and *n*-butyl alcohols, into the corresponding *d*-mannosides (cf. A., 1923, i, 497). E. E. T.

The Separation of the Anti-neuritic Vitamin by Means of its Picrate. G. Bertrand and A. Seidell (*Bull. Soc. Chim. biol.*, 1923, **5**, 794—796).—The crude extract containing the active material is separated from inorganic substances as far as possible, dissolved in 60% alcohol and treated with a solution of picric acid in methyl alcohol. The crude picrate thus obtained is active in amounts of 2 mg. per diem when added to a diet of polished rice and administered to pigeons. On recrystallisation of the picrate from water two separate substances are obtained; one crystallises in needles, m. p. 202°, and is inactive; the other forms a crystalline powder, m. p. 160°, and is active. C. R. H.

Additive Products of the Phosphineimines. M. Masriera (*Anal. Fis. Quím.*, 1923, **21**, 418—435; cf. Staudinger and Hauser, A., 1922, i, 68).—The constitution of the additive products formed from phosphineimines and alkyl or acyl chlorides is discussed. Triphenylphosphinephenylimine reacts with acetyl chloride in ethereal solution, giving a white *compound* to which the formula $PPh_3{:}NPhAcCl$ is assigned. It is unstable and gives on decomposition acetanilide and triphenylphosphine oxide. The additive *compound* of triphenylphosphinephenylimine with methyl iodide is a white substance having m. p. 235°. Attempts to obtain addition of a second molecule of methyl iodide were unsuccessful. The additive *compound* of toluene-*p*-sulphonyl chloride with triphenylphosphineimine is a white, crystalline substance which decomposes when heated, forming resins. On keeping a mixture of triphenylphosphinephenylimine and toluene-*p*-sulphonyl chloride in ethyl-alcoholic solution for three months, two substances are obtained, namely, *triphenylphosphine*-p-*toluenesulphonylphenylammonium hydroxide*, $PPh_3{:}NPh(SO_2{\cdot}C_6H_4Me){\cdot}OH$, a white crystalline substance, m. p. 191°, and its *isomeride*, for which the formula

$$OH{\cdot}PPh_3{\cdot}NPh{\cdot}SO_2{\cdot}C_6H_4Me$$

is suggested; it is crystalline and has m. p. 115°. G. W. R.

The Syntheses of Arsenic Acids by Means of Diazonium Salts. Z. FÖLDI (*Ber.*, 1923, **56**, [*B*], 2489—2498).—Evidence is adduced in favour of the view that the diazonium arsenite is the primary product of Bart's arsinic acid synthesis (cf. Schmidt, A., 1920, i, 897). The transformation of the arsenious ion into the arsinic group is simply explained in accordance with Werner's theory if the constitution $H\left[\begin{matrix}OH\\HO\cdot AsOH\\OH\end{matrix}\right]$ or $H\left[OAs\begin{matrix}OH\\OH\end{matrix}\right]$ is assigned to arsenious acid, and it is regarded as functioning as a monobasic acid, as is generally the case towards alkali kations including the diazonium-ion. In arsenious acid, the arsinic group exists therefore preformed. The production of the arsinate can therefore be explained by assuming that the diazonium kation present in the second sphere of the central arsenic atom enters the first sphere thereby transforming the tervalent into quinquevalent arsenic atom and that the diazoarsinic acid decomposes with evolution of nitrogen.

p-Toluidine is diazotised in hydrochloric acid solution by means of sodium nitrite; the cooled solution is saturated with hydrogen chloride, filtered to remove the precipitated sodium chloride, and treated with arsenic chloride, whereby a paste of colourless, granular crystals is produced without evolution of nitrogen. The product can be coupled with phenols or amines, thus showing the diazonium group to be intact. The addition of alkali hydroxide to the aqueous solution causes immediate evolution of nitrogen and the development of the colours and odours characteristic of Bart's reaction. In the presence of sodium hydrogen carbonate, the arsenious acid can be titrated with iodine, the end-point being shown by the formation of a dark coloured diazonium periodide. According to experimental conditions, the *compounds* $C_6H_4Me\cdot N_2Cl,AsCl_3$, $C_6H_4Me\cdot N_2Cl,2AsCl_3$, $C_6H_4Me\cdot N_2Cl,AsCl_2\cdot OH$, and $C_6H_4Me\cdot N_2Cl,AsCl_3,AsCl_2\cdot OH$ can be obtained. The first two of these are extremely labile and particularly sensitive to moisture; they can only be obtained from solutions which are completely saturated with hydrogen chloride. The fourth substance has m. p. 94—98° (decomp.); it readily loses hydrogen chloride and passes into the *pentachloro*-salt, $C_6H_4Me\cdot N_2(As_2Cl_5O)$, pale pink octahedra, m. p. 111—112° (decomp.), whereas when its solution in absolute alcohol is treated with anhydrous ether it gives the compound $C_6H_4Me\cdot N_2Cl,AsCl_2\cdot OH$, colourless crystals, m. p. about 90° (decomp.). The *salt*, $C_6H_4Me\cdot N_2(AsBr_3\cdot OH)$, m. p. 105°, is described. The hydroxy-chloro-salts can also be prepared from solid *p*-toluenediazonium chloride and arsenic trichloride in concentrated, absolute alcoholic solution.

The diazonium chloroarsenites decompose vigorously in aqueous or alcoholic solution, or in suspension in organic media with evolution of nitrogen in the presence of Gattermann's copper powder or cuprous chloride. In alcoholic solution, the reaction is very complex, giving di-*p*-tolyl, *p*-tolyl ethyl ether, arsenic acid, *p*-tolylarsinic acid, ethyl *p*-tolylarsinate, and *p*-tolylchloroarsine.

A study of the action of *p*-toluenediazonium sulphate on barium arsenite in the presence of water shows that diazonium arsenites are capable of existence in aqueous solution in the presence of an excess of arsenious acid, but attempts to obtain them in the solid state were not successful. Attempts to prepare solutions of diazonium arsenites in the absence of excess of arsenious acid are rendered difficult by the impossibility of preparing undecomposed diazonium hydroxide solutions. When, however, solutions of *p*-toluenediazonium sulphate, barium hydroxide, and arsenious acid in the molecular proportion 1 : 1 : 1 are mixed a pale yellow, turbid alkaline solution is obtained which is alkaline towards litmus but gradually becomes acidic; decomposition of the diazonium arsenite is shown to occur in accordance with the two schemes:

$2C_6H_4Me\cdot N_2\cdot O\cdot As(OH)_2 = C_6H_4Me\cdot AsO(OH)\cdot O\cdot N_2\cdot C_6H_4Me + N_2 + As(OH)_3$ and

$2C_6H_4Me\cdot N_2\cdot O\cdot As(OH)_2 = C_6H_4Me\cdot N_2\cdot AsO(OH)\cdot O\cdot N_2\cdot C_6H_4Me + As(OH)_3$,

the second being the more important. H. W.

Physiological Chemistry.

The Influence of Various Carbohydrates and Amino-acids on the Blood and Urinary Sugar of the Healthy Organism. A. Schätti (*Biochem. Z.*, 1923, **143**, 201—220).—In general, the ingestion by normal individuals of 20 g. of the following carbohydrates produces a hyperglycæmia the intensity of which diminishes in the order given: dextrose, lævulose, sucrose, lactose, galactose. The same amounts of starch, glycine, and alanine produce no hyperglycæmia, but after the ingestion of 100 g. of starch the rise in blood-sugar is as great as, but more delayed than, that produced by 100 g. of dextrose. Peptone and coffee give no hyperglycæmia. Lævulose is excreted more quickly and in greater amount than dextrose, and the sugar excreted after ingestion of sucrose consists chiefly of lævulose. Galactose seems to be excreted largely unchanged by the kidneys. Glycosuria following ingestion of dextrose increases with increasing hyperglycæmia, but the former shows a more delayed maximum than the latter. Glycosuria is not dependent on diuresis, but is regarded as a secretory process. J. P.

Blood-clotting as an Agglutination Process. E. Hekma (*Biochem. Z.*, 1923, **143**, 105—110).—A theoretical paper in which the view is advanced, as a result of the author's previous work, that fibrin formation is a crystallisation process involving the dehydration and agglutination of fibrinogen amicrons. Thrombin is regarded, not as a fibrin ferment, but as an agglutinin, and fibrin consists of fibrinogen plus agglutinin. J. P.

The Influence of Chemicals on Erythrocyte Membranes by Changes in Corpuscular Volume. B. S. NEUHAUSEN and J. E. BRESLIN (*Bull. Johns Hopkins Hosp.*, 1923, **34**, 199—201).—A study of the effects of the salts of the blood and of dextrose on the erythrocyte membranes as shown by a comparison of cell volumes in iso-osmotic solutions. Ions cause swelling in the order, Ca < Na < K. The contracting action of calcium, as opposed to the swelling action of potassium, is specially pointed out. In the case of blood-corpuscles, the membranes are very complex colloidal mixtures, the swelling or precipitation of any component of which will loosen the whole structure.

CHEMICAL ABSTRACTS.

The Rôle of Pancreatic Juice in the Digestion of Proteins. Relative Importance of Trypsin and Erepsin. E. F. TERROINE and ST. J. PRZYLECKI (*Arch. internat. physiol.*, 1923, **20**, 377—396; *Ber. ges. Physiol.*, 1923, **20**, 64; from *Chem. Zentr.*, 1923, iii, 1290).—Pancreatic juice not activated by kinase attacks the normal products of gastric digestion. With activation by kinase, the action is increased. The relative importance of erepsin and trypsin depends on the degree of previous gastric digestion; where this is small, trypsin plays the more important part, but is less important where gastric digestion is more complete. As pancreatic digestion proceeds, the effect of trypsin recedes relative to that of erepsin.

G. W. R.

Effect of Magnesium Sulphate and Metallic Magnesium on Metabolic Exchanges. R. REDING and A. SLOSSE (*Compt. rend. Soc. biol.*, 1923, **88**, 644—646; from *Chem. Zentr.*, 1923, iii, 1108).—Intramuscular injection of 70 c.c. of 10% magnesium sulphate solution decreases the output of total nitrogen, uric acid, and sodium chloride, whilst the output of magnesium is increased. In a rectal carcinoma, injection of 20 c.c. of 10% magnesium sulphate solution was followed by decreased output of total nitrogen, amino-nitrogen, and sodium chloride, and increased output of uric acid and creatine. Similar effects were observed in a rabbit after introduction under the skin of a piece of metallic magnesium.

G. W. R.

The Internal Secretion of the Genital Organs. I. The Genital Organs and Carbohydrate Metabolism. S. TSUBURA (*Biochem. Z.*, 1923, **143**, 248—290).—Castration has no effect on the blood-sugar of fasting dogs, but in the sexually mature animal the operation produces a lowered sugar tolerance. The same effect is produced by ligature of one spermatic cord and extirpation of the opposite testicle, by ligature of both cords, or by exposing the genital glands to *X*-rays. These operations produce a degeneration of the sperm-cells, but do not affect the interstitial cells. The lowered sugar tolerance may be temporarily raised by transplantation of the sexual organs of another animal, but not by feeding the organs or by injection of extracts. Glycogen formation, glycogenolysis, and glycolysis of the blood-sugar in vitro are somewhat delayed after castration, but the blood amylase is unchanged.

After castration, the reactions of the blood-sugar to adrenaline, diuretin, and pituitrin are increased, but thyroid feeding has no effect, although it raises the low sugar tolerance of the castrated animals. The kidneys of the latter are more permeable to sugar, but the excretion of phenolsulphonephthalein is delayed as compared with the normal condition. In general, parallel experiments on male and female dogs gave similar results. The other endocrine organs show alterations after castration, and the observed results may not be wholly due to disturbances of the internal secretory functions of the genital organs. J. P.

The Internal Secretion of the Genital Organs. II. The Genital Organs and Respiratory Gaseous Metabolism. S. TSUBURA (*Biochem. Z.*, 1923, **143**, 291—322).—Castration produces a lowered gaseous metabolism which becomes apparent about one month after the operation. A similar effect is produced by ligature of one spermatic cord and removal of the opposite testicle. Transplantation of the testes of another animal raises the gaseous exchange whilst feeding experiments are ineffective. Dogs in heat show no increased gaseous metabolism. Thyroid feeding raises the low gaseous exchange of castrated animals. The combined results of thyroid feeding on the sugar tolerance (cf. preceding abstract) and gaseous metabolism of castrated dogs are explained as being due to a moderate stimulation of the sluggish carbohydrate metabolism by the thyroid hormone. J. P.

The Ferments in the Placenta. K. MAEDA (*Biochem. Z.*, 1923, **143**, 347—364).—Extracts of the placenta contain diastase in considerable amount, in part derived from the parental blood. Carboxylase and small quantities of lactase and invertase are present, but glycolytic enzymes are not found. Of proteolytic enzymes, erepsin, a weak trypsin, and traces of pepsin, but no rennin, are found. An asparagine deaminase is present. Mono- and tributyrases are found, and the latter, being stable to both quinine and atoxyl, is thus differentiated from serum lipase. Histozyme, a feeble salicylase, and an oxydase acting on pyrocatechol, adrenaline, and dihydroxyphenylalanine, but not on tyrosine, are present.

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The Site of Origin of Bilirubin. A. R. RICH (*Bull. Johns Hopkins Hosp.*, 1923, **34**, 321—329).—Hæmoglobin introduced into the blood-stream of a dog without a liver, and circulating actively for as long as five and a half hours is not transformed into bilirubin. Since, however, the production of bilirubin from circulating hæmoglobin takes place rapidly and readily in a dog with a liver through which the blood-stream passes, it is concluded that the liver is necessary for the transformation of circulating hæmoglobin into bilirubin. The conclusions are applicable only to hæmoglobin circulating in the blood-stream, not to hæmoglobin liberated into the tissues from extravasated blood; the conversion of hæmorrhage hæmoglobin into bilirubuin (hæmatoidin) is a purely local phenomenon, the exact mechanism of which is unknown.

CHEMICAL ABSTRACTS.

[Fish] Liver Oils. M. TSUJIMOTO (*J. Chem. Ind. Japan*, 1923, 26, 482—486).—The oil from the Jewfish (*Stereolepis ischinagi* (Hilg.), contains a large amount of peculiar unsaponifiable matter (up to 50%), which is a viscous substance of reddish-orange colour, having a resinous odour, and showing much resemblance to colophony when dried at 100° for several hours. The name "liver-resin" is proposed for it. Liver oil from *Erilepis zonifer* (Lock.) also contains a similar substance (about 4%). These oils and the unsaponifiable matter (especially in carbon disulphide solution) give a deep violet coloration with sulphuric acid. With a sample of *S. ischinagi* liver oil, the coloration was observed to be about one hundred times as strong as that of a cod-liver oil. K. K.

The Highly Unsaturated Acids in Cod-liver Oil. M. TSUJIMOTO and K. KIMURA (*J. Chem. Ind. Japan*, 1923, **26**, 1162).—By the potassium salt–ether method, and the lithium salt–acetone method, a mixture of highly unsaturated acids was obtained. By converting it into the methyl ester, a fraction (about 4% of the oil) boiling at 220—226°/5 mm. was isolated. The analysis of the ester and the fatty acid from the ester gave $C_{22}H_{33}O_2Me$ and $C_{22}H_{34}O_2$ respectively, and behenic acid was produced from the latter by hydrogenation. Cod-liver oil therefore contains a large amount of clupanodonic acid, $C_{22}H_{34}O_2$. The part of the methyl ester boiling below 220°/5 mm. is supposed to contain a large amount of a highly unsaturated acid containing eighteen or twenty carbon atoms. K. K.

Further Studies on Autoxidations and Oxido-reduction Processes. V. E. ABDERHALDEN and E. WERTHEIMER (*Pflüger's Archiv*, 1923, **200**, 176—193; from *Chem. Zentr.*, 1923, iii, 1290).—The reducing power of muscle in which thermal rigor has been induced is three or four times that of normal muscle. In chemical rigor and rigor mortis, there is a similar increase in reducing power. An increase also occurs during normal or tetanic contraction. It is supposed that such increases are associated with the presence of a thiol group in the muscle fibres. Cysteine serves as a hydrogen carrier and acceptor. A scheme for a stable oxido-reduction system is given. G. W. R.

A Methylation Function of the Thyroids and the Biological Significance of Iodine. B. STUBER, A. RUSSMAN, and E. A. PROEBSTING (*Biochem. Z.*, 1923, **143**, 221—234).—If guanidineacetic acid be administered intravenously to young dogs, an increase of blood creatine–creatinine follows. No such increase occurs in thyroidectomised animals, but if these be given dried thyroid or potassium iodide per os, before the injection of guanidineacetic acid, they react like the normal animals. The blood of normal dogs, but not of thyroidectomised dogs, is also effective in this respect. It is concluded that the capacity of the organism to methylate guanidineacetic acid, and so form creatine and creatinine, is dependent on the integrity of the thyroids, and that iodine compounds are necessary for this methylation process. J. P.

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The Oxytocic–Pressor–Diuretic Principle of the Infundibular Portion of the Pituitary Gland. J. J. ABEL, C. A. ROUILLER, and E. M. K. GEILING (*J. Pharm. exp. Ther.*, 1923, **22**, 289—316).—After a purification of the gland material by precipitation with mercuric chloride, phosphotungstic acid, and tannic acid in succession, the residue is dissolved in an alcoholic solution of tartaric acid and re-precipitated with ether. The resulting precipitate is called the tartrate of the active principle. Its action on the isolated uterus of the guinea-pig may be as much as 1,250 times as great as that of histamine phosphate, whilst it also retains the diuretic and pressor action characteristic of the pituitary extract. C. R. H.

Anaërobic Processes Involved in Muscular Activity. W. HARTREE and A. V. HILL (*J. Physiol.*, 1923, **58**, 127—137).—In muscle, 0·1% of lactic acid can be produced so rapidly by exercise or by stimulation that no appreciable escape of carbon dioxide or of acid is possible. Hence if the hydrogen-ion concentration inside a muscle is not to rise to an excessive degree during exercise, there must be some buffer in it, much more effective than a bicarbonate solution. Meyerhof (*Pflüger's Archiv*, 1922, **195**, 22) has emphasised that in a frog's muscle the absolute amount of bicarbonate present, as determined from the carbon dioxide driven out from the muscle by excess of acid, is quite inadequate to neutralise the lactic acid liberated in severe stimulation. Even if all the carbon dioxide were driven out, only one-seventh to one-tenth of the lactic acid could be neutralised.

The authors further calculate that the 0·3% inorganic phosphate in muscle (a mixture of KH_2PO_4 and K_2HPO_4) is also quite inadequate to keep the P_H within the extreme limits observed, viz., a change from 7·5 to 6·9). Bicarbonate and phosphate together are insufficient to neutralise half the lactic acid formed. There must be, as Meyerhof assumes, some other powerful buffer, doubtless an alkali–protein salt. The addition of lactic acid to shed blood also produces only a fraction of the change in the hydrogen-ion, which would result in a bicarbonate solution of the same concentration; here also alkali protein must play a considerable part.

The authors confirm the existence of a secondary maximum in the production of heat in a muscle in the absence of oxygen; this maximum occurs after about two and a half minutes (see the following abstract for its interpretation). A "balance sheet" is given of the heat evolved in the different phases of muscular contraction; it shows that during the recovery process something between 1/4·7 and 1/6 of the lactic acid removed is oxidised, the rest being reconverted into glycogen. G. B.

Heat of Combustion of Glycogen in Relation to Muscular Contraction. W. K. SLATER (*J. Physiol.*, 1923, **53**, 163—167).—Glycogen (from *Mytilus edulis*, a convenient source) only becomes anhydrous at 100° in a vacuum over phosphoric oxide (cf. Harden and Young, T., 1902, **81**, 1224). Dried by the method of Atkins and Wilson (T., 1915, **107**, 916), it has the composition $(C_6H_{10}O_5,H_2O)_n$.

The heat of combustion seems previously to have been determined with slightly hydrated material. The author finds the heat of combustion of hydrated glycogen to be 3,883 cal. per gram, which is about 100 cal. higher than that calculated from Stohmann and Schmidt's value, 4,190 (A., 1895, ii, 102), for (presumably imperfectly) dehydrated glycogen, for this would give for the hydrated form $162/180 \times 4{,}190 = 3{,}771$ cal. The heat of wetting is found to be about 9 cal., hence the heat of combustion of hydrated glycogen in solution is 3,874 cal. The heat of combustion of lactic acid is, according to Meyerhof, 3,601 cal., leaving 273 cal. for the conversion of 1 g. of glycogen into 1 g. of lactic acid. The heat of neutralisation of lactic acid by acid salts is, according to Meyerhof (*loc. cit.*), 19 cal. per g., which leads to the value $273 + 19 = 292$ cal. for the heat liberated during contraction and relaxation of a muscle, per g. of lactic acid formed. The total initial heat, given by Hartree and Hill in their balance-sheet (as the result of physical measurement, see preceding abstract) is 296 cal., in close agreement with that calculated above. The salt buffering of the lactic acid is, however, probably only of a temporary character and is replaced by the more efficient buffering by alkali-protein. Meyerhof has shown that the neutralisation of 1 g. of lactic acid by alkali-protein produces 138 cal., or 119 more than that by salts. The whole of these 119 cal. are, however, not produced; according to Hartree and Hill the delayed anaërobic heat production is 74 cal. per g. of lactic acid, so that only about 60% of the lactic acid formed is neutralised by alkali protein (the rest remains neutralised by salts). The delayed heat production, presumably due to a transfer of alkali from protein to acid phosphate and carbonic acid, is the cause of the secondary maximum in the heat production occurring after two and a half minutes (preceding abstract). The velocity of this reaction is independent of the temperature, and thus probably depends on a physical process (rate of diffusion of acid phosphate- and carbonic acid-ions) through the muscle-tissue. This theory demands some special distribution of phosphate and carbonate molecules in the muscle substance, and may be represented by the following scheme :

Contraction (*a*) Glycogen $\longrightarrow$ lactic acid; (*b*) lactic acid and contractile mechanism produce mechanical response.

Relaxation (*a*) Lactic acid + K_2HPO_4 and $KHCO_3 \longrightarrow$ K lactate + KH_2PO_4 and H_2CO_3.

Anaërobic recovery (*a*) KH_2PO_4 and H_2CO_3 + K protein $\longrightarrow$ $K_2HPO_4 + KHCO_3$ + H protein. G. B.

Products of the Catalytic Hydrolysis of Horse Hair. V. S. Sadikov (*Biochem. Z.*, 1923, **143**, 504—511).—Fractionation of the product obtained by the catalytic hydrolysis of horse hair under pressure yielded the following substances : (1) A peptide anhydride (m. p. 258°) of alanine and leucine to which the formula $C_{21}H_{36}O_4N_4$ or $C_{21}H_{38}O_4N_4$ is ascribed. (2) A peptide anhydride of alanine and leucine (m. p. 260°) of the formula $C_9H_{16}O_2N_2$. (3) A peptide anhydride of leucine and valine (m. p. 246°) of the formula

$C_{11}H_{20}O_2N_2$. (4) Butylalanyl-leucine anhydride, $C_{10}H_{18}O_2N_2$, or its unsaturated derivative, $C_{10}H_{16}O_2N_2$ (m. p. 224°). (5) Diketomethylpiperidine, $C_6H_9O_2N$ (m. p. 196°). (6) A cyclic nitrogen substance, $C_{15}H_{30}N$, of an alkaloidal nature. (7) A substance of the formula $C_{13}H_{20}O_3N_2$ (m. p. 170°). Various other less well characterised derivatives of the nature of diketopiperazines and keto- and diketo-piperidines were obtained. J. P.

Calcium Fixation by Animal Tissues. IX. E. FREUDENBERG and P. GYÖRGY (*Biochem. Z.*, 1923, **142**, 407—416).—A study has been made of the extent to which calcium phosphate and carbonate are formed, when solutions of casein and egg-albumin are treated with sodium phosphate or carbonate at different p_H, and dialysed against calcium chloride. After dialysis the distribution of calcium, phosphate, and fixed carbon dioxide was determined both externally and internally, and the bearing of the results on the process of calcification occurring in animal tissues is discussed. The conclusion is drawn that a reversible fixation of calcium by the tissue proteins takes place. With diminishing metabolic activity, the fixed calcium reacts with phosphate and carbonate to give rise to complex protein–calcium–phosphate–carbonate compounds from which the carbonate is gradually eliminated by the acid nature of the proteins under tissue conditions. The excess of calcium phosphate is then split off, leaving the original active group of the protein free to combine with more calcium (cf. also György, this vol., i, 120). J. P.

The Basis of the Oxidation Theory of Wieland. O. WARBURG (*Biochem. Z.*, 1923, **142**, 518—523).—A criticism of Wieland's views on the mechanism of oxidation. In place of the theory that organic oxidations proceed in two phases, first hydration followed by abstraction of hydrogen by interaction with molecular oxygen, the theory advanced by the author supposes that molecular oxygen is first activated by combination with a catalyst (iron, platinum, or organic catalyst) and then reacts directly with the oxidisable substance. It is argued that Methylene-blue, quinone, etc., do not react like molecular oxygen when substituted for the latter (Wieland, A., 1913, i, 1304), but as activated oxygen, *i.e.*, molecular oxygen + catalyst. The action of hydrocyanic acid in inhibiting oxidations is regarded as opposing Wieland's theory, whilst it receives a ready interpretation on the author's views, since it combines with the catalyst (*e.g.*, iron) and prevents the activation of the oxygen. J. P.

Carnisapidine in Animal Tissues. F. BATTELLI and L. STERN (*Compt. rend. Soc. Biol.*, 1923, **88**, 575—577; from *Chem. Zentr.*, 1923, iii, 1037).—The constituent of animal tissues to which the taste is due is named by the author *carnisapidin*. The amount present in different tissues was determined approximately by dilution of extracts until the taste was just perceptible. The highest content was found in muscles, liver, spleen, and kidneys, lower amounts were found in the thymus, brain, and lungs. G. W. R.

Sarcochromogen in Animal Tissues. F. BATTELLI and L. STERN (*Compt. rend. Soc. Biol.*, 1923, **88**, 679—681; from *Chem. Zentr.*, 1923, iii, 1037; cf. preceding abstract).—Aqueous extracts of animal tissues contain a sarcochromogen which differs from sarcochrome in not being precipitated by metaphosphoric acid. Sarcochromogen is not changed into sarcochrome on evaporation to dryness if the temperature remains below 80°. G. W. R.

The Rôle of Carnisapidin and Sarcochromogen in Animal Tissues. L. STERN and F. BATTELLI (*Compt. rend. Soc. Biol.*, 1923, **88**, 681—683; from *Chem. Zentr.*, 1923, iii, 1037; cf. preceding abstracts).—The occurrence of carnisapidin and sarcochromogen in animal tissues appears to have no direct correlation with metabolic exchange. Certain proteins such as casein give, on treatment with pepsin, substances analogous to sarcochromogen. Carnisapidin and sarcochromogen are easily dialysable, and are not attacked by digestive ferments. Carnisapidin, administered intravenously, is eliminated in the urine, but when administered orally or subcutaneously it is retained or decomposed, probably in the liver. G. W. R.

The Extractives of *Actinia equina*. D. ACKERMANN, F. HOLTZ, and H. REINWEIN (*Z. Biol.*, 1924, **80**, 131—136; cf. A., 1923, i, 1155).—The extractives of *Actinia equina* were subjected to fractionation by Kossel and Kutscher's method. The histidine and arginine fractions have not yet been worked up. In the purine fraction there was obtained adenine, isolated in the form of its picrate. From the lysine fraction there was obtained (1) tetramethylammonium hydroxide (as picrate); (2) a base, identified as pyridylmethylammonium hydroxide (*chloroaurate*, m. p. 252—253°, and *chloroplatinate*); (3) a base of unknown constitution, ***actinine***, $C_{13}H_{24}O_5N_2$; from it there were prepared a *chloroaurate*, m. p. 169°, a *chloroplatinate*, dark red, crystalline nodules, decomp. 209°, and a *hydrochloride*, m. p. 207—208°. C. R. H.

The Chemical Differential Diagnosis of Transudates and Exudates. K. HIRUMA (*Biochem. Z.*, 1923, **142**, 506—517).—Exudates contain an albumin precipitable by an acetate mixture at C_H $0{\cdot}36 \times 10^{-4}$, by a phosphate mixture at C_H $0{\cdot}214 \times 10^{-2}$, and by a citrate mixture at C_H $1{\cdot}13 \times 10^{-4}$. Inflammatory cerebrospinal fluids contain the same type of albumin as the exudates formed in pleurisy and in peritonitis. The average sugar content of transudates is 0·115% and of exudates 0·07%, the former being in general above the plasma sugar value of the patient, and the latter somewhat lower. The residual nitrogen of transudates, and the amino-nitrogen and ammonia of both transudates and exudates, are approximately the same as those of the blood, whilst the residual nitrogen of exudates is higher than that of transudates. In nephritis, the residual nitrogen is greater the more marked is the œdematous condition. J. P.

The Distribution of Nitrogen in the Urine of Young Dogs and its Dependence on Diet. F. SERIO (*Biochem. Z.*, 1923, **142**, 440—453).—The distribution of nitrogen in the urine of young dogs

kept on a diet rich in fat but poor in, or free from, nitrogen is similar to that of starved animals. The urea is diminished and the ammonia increased due to starvation acidosis. The excretion of amino-acids is not influenced by a low nitrogen diet, but it is lowered on a milk diet. The "urease" method for estimating urea gives lower results than the Mörner-Sjöquist method, a difference which is more marked the smaller the ratio of urea nitrogen to total nitrogen becomes. During the period of pre-mortal increase in the nitrogen excretion, the difference disappears, and it is less apparent on a milk diet. The suggestion is made that the difference is due to allantoin and creatinine being estimated along with urea in the Mörner-Sjöquist method, and that the excretion of these urinary constituents varies under the conditions studied, ceasing during the pre-mortal period. J. P.

Sulphatase. III. The Enzymatic Fission of the Ethereal Sulphates in the Urine of the Horse, Camel, and Dog. J. NOGUCHI (*Biochem. Z.*, 1923, **143**, 186—189).—By treating horse and camel urine with preparations of sulphatase at 37°, hydrolysis of the ethereal sulphates varying from 60 to 90% was obtained. Similar extensive hydrolysis of the organic sulphates occurred in the urine of a dog to which phenol had been administered. J. P.

Acetonuria and Acidosis. D. ADLERSBERG (*Biochem. Z.*, 1923, **143**, 527—532).—From a study of the effect of orally administered ammonium dihydrogen phosphate on normal subjects kept on a diet free from carbohydrate, and on diabetic subjects, it is concluded that acidosis diminishes the urinary excretion of ketone substances in these conditions. J. P.

Thymolglycuronic Acid. K. TAKAO (*Z. physiol. Chem.*, 1923, **131**, 304—306).—According to Blum (A., 1892, 1116), thymol is not excreted by the dog as thymolglycuronic acid, although it is so in man. It is now shown, however, that a very small fraction of it is so excreted by the dog. By treatment with sodium hypochlorite and fuming hydrochloric acid, thymolglycuronic acid in the urine was converted into *dichlorothymolglycuronic acid*, $C_{16}H_{22}O_8Cl_2$, colourless needles, m. p. 118—119°, $[\alpha]_D^{20}$ −66·46° ($c = 3{\cdot}9497\%$) (*barium* salt, $[C_{16}H_{21}O_8Cl_2]_2Ba$). W. O. K.

Phosphorus Metabolism in Avitaminosis. K. MORINAKA (*Biochem. Z.*, 1923, **142**, 381—384).—The phosphorus content of the livers of avitaminosed rats to which sodium phosphate, lecithin, or phosphoprotein has been administered does not differ appreciably from that of the livers of similarly fed normal rats. The conclusion is drawn that in avitaminosis the soft tissues do not lose their power of phosphorus retention. J. P.

The Kephalin and Lecithin Content of the Brain in Avitaminosis. H. NAITO (*Biochem. Z.*, 1923, **142**, 385—392).—The percentage content of kephalin and lecithin in the brains of avitaminosed rats and guinea-pigs does not depart appreciably from normal, although there is a diminution in the total mass of brain-tissue. J. P.

The Lecithin Content of the Brain and Liver of Normal and Avitaminosed Pigeons after Forced Lecithin Feeding. H. NAITO (*Biochem. Z.*, 1923, **142**, 393—397).—Lecithin feeding slightly increases the amount of the lipoid found in the livers of normal, but not in the livers of avitaminosed pigeons. The lecithin of the brain is not affected in either case. It is concluded that in the avitaminosed liver, phosphorus compounds other than lecithin increase at the expense of the latter (cf. Morinaka, above). J. P.

Fat Metabolism in Avitaminosis. IV. The Gaseous Metabolism of Starved Avitaminosed Rats during Digestion and after Adrenaline Injection. K. ASADA (*Biochem. Z.*, 1923, **143**, 387—398).—The oxygen consumption of partly and completely avitaminosed rats is sub-normal, both during a period of starvation and while a vitamin-free meal is being digested. The extent of the increase observed under the latter conditions compared with the requirements of the starved animals varies inversely with the severity of the avitaminosis. Adrenaline injections produce a greater increase in oxygen consumption in avitaminosed than in normal rats. A discussion is appended of the earlier results obtained in the study of carbohydrate and fat metabolism in avitaminosis. J. P.

Uric Acid and Allantoin Metabolism in Avitaminosis. A. ADACHI (*Biochem. Z.*, 1923, **143**, 408—422).—In avitaminosis, the excretion of allantoin in dogs shows no notable variations, whilst that of uric acid is variable and may show transitory increases. In long-continued avitaminosis, the uric acid excretion is markedly increased and may reach values three times those obtained in normal animals. It is concluded that an increased consumption of nucleins occurs in the later stages of avitaminosis. J. P.

The Pharmacology of the Rare Earths. I. Cerium. S. HARA (*Arch. expt. Path. Pharm.*, 1923, **100**, 217—253).—In general, cerium bears a close resemblance to aluminium and to the heavy metals in its pharmacological action. Proteins are precipitated by moderate but not by strong concentrations of its salts. C. R. H.

The Pharmacology and Toxicology of Carbon Tetrachloride. P. D. LAMSON, G. H. GARDNER, R. K. GUSTAFSON, E. D. MAIRE, A. J. MCLEAN, and H. S. WELLS (*J. Pharm. expt. Ther.*, 1923, **22**, 215—288).—A comprehensive study of the pathological effects following administration to dogs of carefully purified carbon tetrachloride. Oral administration produced only slight and transitory symptoms unless accompanied or preceded by administration of fats or alcohol. When given intravenously, it is lethal in doses of 0·154 c.c. per kg. body-weight.

The pathology of carbon tetrachloride poisoning consists essentially (apart from local irritant effects such as bronchitis following inhalation) in damage done to the liver, one of the first indications of which is the appearance of abnormal amounts of bilirubin in the blood. C. R. H.

The Rôle of certain Carbohydrates in the Organism. E. O. FOLKMAR (*Bibliotek laeger*, 1923, **115**, 120—125; from *Chem. Zentr.*, 1923, iii, 1291).—With continued intravenous injection of pentoses in small amounts at a rate comparable to intestinal absorption, approximately one-half is excreted in the urine. Galactose can be assimilated at the daily rate of 1—2 g. per kg. of live weight without glycosuria or appreciable increase in blood-sugar. Maltose is well utilised, after becoming hydrolysed by maltase. There is an appreciable retention of sucrose in certain circumstances; invertase is, however, not present in blood. Raffinose is completely excreted. The small amounts of ethyl alcohol normally present in blood are attributed to casual decomposition of carbohydrates and not to the action of an alcoholase. G. W. R.

The Influence of Oral Administration of Dextrose on the Blood-sugar and on Glycosuria in Healthy Individuals. G. CONSTAM (*Biochem. Z.*, 1923, **143**, 75—104).—The elimination of sugar in the urine is best followed by estimating the amount excreted in unit time. Observations based purely on changes in concentration do not give dependable results. In normal individuals a mixed meal is followed by a definite glycosuria. Tap water produces a dilution glycosuria which reaches a maximum in about one hour. The assimilation limit for sugar in the same individual is variable and is higher after five hours' than after fourteen hours' abstention from food, whilst the assimilation capacity varies in the opposite sense. In the cases quoted, the tolerance lay between 100 and 150 g. of dextrose in 500 c.c. of water after five hours, and between 20 and 30 g. in the same volume after fourteen hours' starvation; less concentrated solutions caused dilution glycosuria which diminished with increasing concentration of dextrose until the assimilation limit was reached, when a true glycosuria supervened. The blood-sugar reaches its maximum about half an hour before the urinary sugar. The suggestion is made that the power of the organism to raise the sugar tolerance is a protective mechanism which prevents loss of sugar during periods of diminished rate of assimilation. J. P.

A New Method of Preparing *s*-Diphenylguanidine. Its Pharmacological Effects. O. RIESSER (*Z. physiol. Chem.*, 1923, **131**, 204—213).—Diphenylguanidine is formed together with a small amount of triphenylmelamine when dicyanodiamine is heated with aniline hydrochloride at 190—200°. It crystallises from alcohol in white needles, m. p. 145—148°, and forms a chloroaurate. The pharmacological action of this substance has been investigated. It increases the reflex irritability and also causes central paralysis. In warm-blooded animals, it causes death by arrest of the respiration. It produces progressive paralysis when applied to isolated frog's muscle. W. O. K.

Chemistry of Vegetable Physiology and Agriculture.

Biology of *Bacillus coli communis*. Attempts at "Dysmutation." O. FERNÁNDEZ and T. GARMENDIA (*Anal. Fís. Quím.*, 1923, **21**, 481—492).—A study of the effect of various reagents on the fermentation of dextrose by *B. coli communis*. Dysmutation consists in the formation of alcohol, acetic acid, and glycerol from sugars through the acetaldehyde formed as an intermediate stage undergoing the Cannizzaro reaction yielding ethyl alcohol and acetic acid. The dysmutation effect, as judged by the amount of acetic acid produced from dextrose was considerable in the case of cultures to which sodium hydrogen carbonate was added. Less appreciable effects were produced where amino-acids were added. G. W. R.

The Decomposition of *d*-Glucosamine by Micro-organisms. K. TAKAO (*Z. physiol. Chem.*, 1923, **131**, 307—318).—*Bacillus subtilis*, grown on a synthetic medium, with or without the addition of peptone, in presence of *d*-glucosamine forms from the latter succinic acid and a small quantity of lactic acid. If a modified medium is used in which no carbonate is present, lactic acid, but no succinic acid is formed. *B. coli* also forms lactic acid and succinic acid, whilst *B. prodigiosus* forms only lactic acid when grown on a synthetic medium containing *d*-glucosamine. W. O. K.

The Sulphur Cycle in Soil. (The Biology of Thiosulphate Bacteria.) G. KLEIN and A. LIMBERGER (*Biochem. Z.*, 1923, **143**, 473—483).—The thiosulphate bacteria present in soil can be cultured aërobically in inorganic or organic media, and are capable of oxidising the various inorganic compounds of sulphur which occur in soils to sulphuric or polythionic acids. They also oxidise the sulphur of cystine, and to a less extent that of albumin and nuclein to sulphuric acid. Sulphur is an intermediate product in all cases and may separate in a crystalline condition. In the presence of potassium nitrate, the oxidation is accompanied by the formation of nitrite and ammonia, whilst the presence of ammonium chloride gives rise to the former. The spores of the bacteria are found in water and air as well as in the soil. Considerable importance is attached to the part played by these bacteria in the sulphur cycle occurring between the plants and animals. J. P.

The Influence of Oxygen on the Assimilatory and Dissimilatory Activity of Yeast. III. The Behaviour of Added Alcohol in a Yeast Suspension. H. LUNDIN (*Biochem. Z.*, 1923, **142**, 454—462).—Arising from the author's previous work (A., 1923, i, 1268), a study has been made of the capacity of aqueous yeast suspensions, containing no carbohydrate or source of nitrogen, to assimilate added ethyl alcohol both under normal conditions and in the presence of excess of oxygen. In contrast to the results

obtained with " nascent " alcohol formed from carbohydrate which is assimilated both with and without excess of oxygen, added alcohol is only assimilated when a stream of oxygen is passed through the solution. Carbohydrate alone is formed and the yeast-cells increase in mass, but not in numbers. On the assumption that no direct oxidation of part of the added alcohol occurs (*loc. cit.*), it is shown that a utilisation of a portion of the assimilated carbohydrate takes place which runs parallel with its formation. A summary is given of the present results, together with the author's earlier observations.

J. P.

The Influence of Oxygen on the Assimilatory and Dissimilatory Activity of Yeast. IV. The Behaviour of certain Organic Acids. H. LUNDIN (*Biochem. Z.*, 1923, **142**, 463—492).—The methods already described (cf. preceding abstract) have been extended to a study of the capacity of a yeast suspension to assimilate various organic acids. The sodium and ammonium salts of citric, malic, tartaric, and succinic acids are not assimilated even in the presence of an excess of oxygen, and the added salts are without influence on the course of self-fermentation of the yeast. Potassium acetoacetate is assimilated more especially in concentrations of about 1%. Potassium carbonate is formed at the same time, and unless the p_H is adjusted the process is arrested. It is supposed that acetone and carbon dioxide are formed, and the former, in the nascent state, is assimilated to form carbohydrate when an excess of oxygen is provided. The newly-formed carbohydrate may then undergo oxidation. As in the previous experiments, carbohydrate alone is formed, and no alteration in the protein constituents of the yeast is noted. J. P.

Carboligase. VI. A New Type of Change of Acetaldehyde by Fermenting Yeast. C. NEUBERG and E. REINFURTH (*Biochem. Z.*, 1923, **143**, 553—565).—The addition of acetaldehyde to dextrose, lævulose, or sucrose undergoing fermentation by top- or bottom-yeasts, leads to the formation of optically active acetylmethylcarbinol, $CH_3 \cdot CH(OH) \cdot CO \cdot CH_3$. This " acyloin " synthesis also occurs in cell-free fermentations. Part of the acetaldehyde undergoing condensation arises from the sugar (cf. A., 1923, i, 973).

J. P.

The Fermentation Co-enzyme (Co-zymase) of Yeast. I. H. v. EULER and K. MYRBÄCK (*Z. physiol. Chem.*, 1923, **131**, 179—203).—Yeast was obtained free from co-enzyme by grinding up the dry yeast with water, centrifuging, again grinding up with water, and centrifuging. The product was then diluted to a given volume with water. A solution of co-enzyme was obtained by boiling yeast with water for a few minutes and if necessary filtering. The co-enzyme is completely precipitated by 50—80% alcohol.

The effect of variation of the p_H on the rate of fermentation of dextrose by various yeasts has been investigated (cf. Euler and Heintze, A., 1920, i, 513). Fermentation is most rapid at p_H 6·2—6·8. Fresh yeast preserves its maximum fermentation over a

greater range of p_H than dried yeast. For autofermentation, the optimum p_H is 5—6. The observation of Harden that the activity is very dependent on the amount of phosphate-ion present is confirmed. The activity is a maximum at a certain optimum phosphate content. If there is a constant amount of washed yeast present, then the activity is at first approximately proportional to the amount of the co-enzyme present, and gradually, with increasing co-enzyme, becomes less than required by this relation, and ultimately is approximately constant. Similarly, if the co-enzyme is constant, the activity is at first approximately proportional to the amount of washed yeast, but with large amounts of washed yeast ultimately constant. In presence of constant quantities of washed yeast and of activator, the fermentation increases with increase in the amount of dextrose present to a maximum, and it then decreases. In the absence of phosphate, arsenate does not cause marked fermentation. The co-enzyme is apparently stable in aqueous solution for at least twenty-three hours, and is dialysable through a collodion membrane. It is precipitable by lead acetate and it is not identical with vitamine-*D* as it is not contained in orange juice or malt extract.

W. O. K.

Is Lactic Acid Produced in Alcoholic Fermentation? A. FERNBACH and M. SCHOEN (*Compt. rend. Soc. Biol.*, 1923, **89**, 475—477; from *Chem. Zentr.*, 1923, iii, 1035).—From the products of the alcoholic fermentation of sucrose in the presence of calcium carbonate, *d*- and *l*-lactic acid were isolated as the zinc salts. The *d*-lactate was in excess.

G. W. R.

Formation of Organic Acids by *Sterigmatocystis nigra* [*Aspergillus niger*] in Unbalanced Media. M. MOLLIARD (*Compt. rend.*, 1924, **178**, 41—45).—Previous work (A., 1922, i, 611) is continued from a more quantitative point of view. Known weights of the fungus were allowed to grow in presence of media of different composition (varying the proportions of sucrose and inorganic salts), and the amounts of citric and gluconic acid produced determined from time to time. It is shown that reduction of the proportion of nitrogen present favours the production of gluconic acid, reduction of the other inorganic constituents of the culture medium (phosphorus, potassium, magnesium, iron, and zinc) causing the formation of oxalic and citric acids.

E. E. T.

Antiseptic Action of the Zinc Chloride Salt of Aniline. J. W. HOWARD and F. D. STIMPERT (*J. Amer. Chem. Soc.*, 1923, **45**, 3106—3108; cf. A., 1899, i, 40; 1911, i, 191; 1912, i, 363).—The salt $(NH_2Ph)_2,ZnCl_2$ was formed by intimately mixing aniline and fused zinc chloride; it melts at 255°, and is soluble to the extent of 0·64 g. in 100 c.c. of water at 20°, 0·87 g. in 100 c.c. of 0·4% hydrochloric acid at 20°, and 0·066 g. in 100 c.c. of 95% alcohol at 20°. It is readily decomposed by *N* sodium hydroxide or boiling water. Tests with a culture of *Staphylococcus aureus* indicate that the salt has greater bactericidal action than either aniline or zinc chloride, the respective relative efficiency being approximately $10:7\frac{1}{2}:2$.

F. B.

The Evolution of Phosphorus during Germination. M. H. VAN LAER and R. DUVINAGE (*Bull. Soc. chim. Belg.*, 1923, **32**, 355—357).—Determinations of the amount of phosphorus and its distribution in the various parts of the grain have been carried out in the case of barley, the grains themselves, the straw, endosperm, seeds, and roots being examined. The grains were first soaked and then allowed to germinate at 15°. The following facts were established: (1) soaking involves an elimination of about 10% of phosphorus; this takes effect both on the straw and on the endosperm; (2) during germination, a migration of phosphorus from the endosperm to the embryo occurs; (3) kilning of the grain has little effect. In the raw barley, the embryo is rich in phosphorus whilst the straw is poor; during germination the phosphorus content of the endosperm diminishes. It is shown that in the embryo, although the amount of phosphorus is greatly increased, the percentage amount remains practically constant, owing to the development of the embryo itself. During germination, a portion of the phosphorus is rendered soluble, and it is this soluble phosphorus which migrates to the embryo. F. G. P.

Theory of Carbonic Acid Assimilation. WO. OSTWALD (*Kolloid Z.*, 1923, **33**, 356—368).—A theoretical paper in which the experimental work on this subject is briefly summarised and the points are noted which must be covered by any theory of assimilation. The following new hypothesis is developed. The primary process of assimilation is a photo-autoxidation, which consists in the formation of a lipoid peroxide sparingly soluble in water. The second process is the formation of an additive compound of albumin and carbon dioxide; this is followed by the interaction of the lipoid peroxide and the albumin–carbon dioxide complex with water in which oxygen is given up, whereby, either, according to Wislicenus's reaction, carbonate is reduced by hydrogen peroxide, or through the formation of an albumin–carbon peroxide compound the reduction through formic acid to formaldehyde takes place. The fourth process consists in the recombination of an oxygen atom with the lipoid oxide to re-form the lipoid peroxide. This combination takes place in the presence of light in chlorophyll-bearing cells and brings the system back to its initial condition. The lipoid peroxide appears to be the "photochemical motor" of the assimilation process. The photochemical reaction in assimilation is not a photo-reduction, but a photo-autoxidation. The whole of the reactions take place in the interface albumin–lipoid, and all work in such a way that the interface is maintained. Chlorophyll appears not to take part in the assimilation process; stoicheiometrically its action probably consists in a physico-chemical promotion of the photo-autoxidation of the lipoid. J. F. S.

Composition of Vegetable Juices obtained by Pressure. G. ANDRÉ (*Compt. rend.*, 1924, **178**, 114—116).—Previously (*ibid.*, 1922, **175**, 286) it was shown that when certain fruit juices are filtered through porous porcelain impregnated with collodion, inorganic, but not organic, phosphorus passed through, whilst the

fraction of the total nitrogen passing through was of the same order as the fraction not coagulable by heating at 100°. The relative proportions of filtrable, coagulable, and total nitrogen remain almost constant during growth in the case of potatoes; with increase of filtration pressure, the ratio inorganic phosphorus : total phosphorus increases, that of total phosphorus to total nitrogen remaining constant. E. E. T

Wood Sap. I. Presence of Enzymes in Wood Sap. II. Variations in the Amount of Oxydases in Wood Sap during the Bleeding Period. E. Ph. Votchal (*Pamphlet*, Moscow, 1916).—The sap in the outer annual rings in healthy trees is completely sterile. Oxydases and diastases are shown to be present. The maximum oxydase content is reached when trees break into leaf. G. W. R.

The Anthocyans in Norton and Concord Grapes. The Chemistry of Grape Pigments. R. J. Anderson (*J. Biol. Chem.*, 1923, **57**, 795—813).—The pigments present in two varieties of American grapes, namely, Norton (*Vitis æstivalis*, *V. labrusca*) and Concord (*V. labrusca*), have been examined by the methods of Willstätter and Zollinger (A., 1915, i, 285; 1917, i, 47). The same anthocyanin chloride, $C_{23}H_{25}O_{12}Cl,3H_2O$, has been isolated from both varieties. On hydrolysis, it yields dextrose and an anthocyanidin chloride, $C_{17}H_{15}O_7Cl,1\frac{1}{2}H_2O$. The substances are identical in composition with the oenin and oenidin chlorides obtained by Willstätter and Zollinger from European grapes (*V. vinifera*), but they differ from these substances in that the anthocyanidin contains only one methoxyl group, whereas oenidin contains two. The colour reactions are, moreover, different. The anthocyanin gives with ferric chloride in aqueous solution a purple colour which quickly fades to light brown, and in alcoholic solution an intense blue which changes to purple and finally to wine-red; the anthocyanidin gives with the same reagent both in aqueous and alcoholic solution a momentary purple colour fading to an almost colourless or faintly yellow solution. Evidence of the presence of a diglucoside has also been obtained. E. S.

Constituents of *Milletia taiwaniana*, Hayata. T. Kariyone, K. Atsumi, and M. Shimada (*J. Pharm. Soc. Japan*, 1923, No. **500**, 739—746).—Nagai (*J. Tokyo Chem. Soc.*, 1902, **23**, 744) isolated rotenone as one of the poisonous constituents of *Milletia taiwaniana*, Hayata, produced in Formosa. Later, Ishikawa (A., 1918, i, 94) isolated anhydroderride from the mother-liquor of rotenone and pointed out that rotenone was not identical with tubotoxin, a poisonous constituent of *Derris elliptica* (*J. Pharm. Soc. Japan*, 1923, No. **491**, 10). The authors have established the identity of rotenone and tubotoxin from the coincidence of the following properties: Crystalline forms (rhombic plates from hot alcohol or needles from benzene); m. p. 163°; (mixed sample gave the same m. p.), empirical formula, $C_{18}H_{18}O_5$, $[\alpha]_D^{20}$ −236·5° to −244°, oxime,

m. p. 245°, and phenylhydrazone, m. p. 255°. The authors have retained the name rotenone, as it was the first proposed. From crude rotenone, a white, wax-like, amorphous substance was isolated; it has m. p. 80°, acid value 15·85, saponification value 33·92 (118·70 after acetylation), and iodine number 17·02. K. K.

The Acids and Red Colouring Matter of the Horned Poppy (*Glaucium luteum*). H. SCHMALFUSS (*Z. physiol. Chem.*, 1923, **131**, 166—167).—The following acids have been obtained from the juice expressed from the horned poppy: citric acid, 25·82%, lactic acid, 18·24%, acetic acid, 11·88%, succinic acid, 1·99%, fumaric acid, 21·59%, malic acid, 13·50%, anhydromalic acid, 5·92%, $\beta\gamma$-dihydroxy-Δ^{β}-butene-$\alpha\delta$-dicarboxylic acid, 1·07%, the steric configuration of which has not been determined, and traces of formic acid. The hydrochloric acid extract of the pulp left contained fumaric acid 34·33%, malic acid 12·53%, and oxalic acid 53·14%. No trace of maleic acid could be detected in the plant. The red colouring matter appears to be a lipochrome. W. O. K.

Lipase in Sunflower (*Helianthus annuus*) Seeds. F. TRAETTA-MOSCA and F. MILLETTI (*Ann. Chim. Applicata*, 1923, **13**, 270—288).—The authors give a summary of the literature dealing with the lipolytic enzymes of seeds and describe experiments which show that sunflower seeds exhibit lipolytic activity, this being only slight in the quiescent seeds, but becoming more intense in germinating and also in de-fatted seeds. Experiments with oleic acid and glycerol yield results showing that the lipase of sunflower seeds exerts also a synthetic action. Acid is liberated in gradually increasing proportions from linseed, cotton-seed, and castor oils by the agency of sunflower seeds. T. H. P.

Phosphate Behaviour in Soils. J. S. BURD and J. C. MARTIN (*Science*, 1923, **58**, 227—228).—By use of the authors' method (*J. Agr. Sci.*, 1923, **13**, 265) for the extraction of what is probably the true soil solution, it has been shown that after a volume of solution equal to the amount of water initially contained in the compacted soil has been removed, the solutions obtained from a second displacement of the same mass of soil with an equal amount of water have decreasing total concentrations of electrolytes, but the phosphate concentrations increase. Thus, at the approach of the end of the growing season, the diminished total concentration in the soil solution is probably accompanied by a tendency towards enhancement of the concentration of phosphate. An apparent result of this effect has been observed, although it may easily become masked by experimental error in soils of low total concentration or by increased absorption of phosphate by the plant in the later stages of growth. A. A. E.